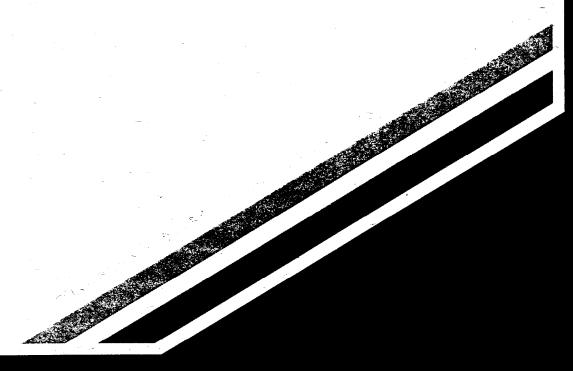




Characterization of Emissions from Nickel Planting

Volume I: Technical Report



CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY



AIR RESOURCES BOARD Research Division

CHARACTERIZATION OF EMISSIONS FROM NICKEL PLATING

VOLUME I – TECHNICAL REPORT

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DISCLAMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

Workplace exposure data were located. According to a study by Crawford (1996a), nickel exposures in the workplace are unknown due to a lack of resources to measure exposure. However, notes Crawford, data from various nickel plating operations are detailed in a health guide published jointly by the Nickel Producers Environmental Research Association (NiPERA) and the Nickel Development Institute (NiDI) (1994). The available data from several nickel plating operations indicate that, while some parts of the nickel plating operations exceed regulations, exposures generally are lower and in compliance with regulations overall. (Crawford, 1996a, p. 66)

Exposure Limits - The permissible exposure limits are different, though similar, from one country to the next. For the United States, the limits set by OSHA are 1 mg/m³ for nickel metal and insoluble nickel compounds and 0.1 mg/m³ for soluble compounds. However, the 0.1 mg/m³ value was rescinded because it had been improperly established. As a result, the only permissible exposure limit for nickel and any of its compounds, except for nickel carbonyl, is 1 mg/m³. (Crawford, 1996a)

The American Conference of Governmental Industrial Hygienists (ACGIH) has put nickel soluble compounds on the "Notice of Intended Changes List for 1996." The intended change was to lower the Threshold Limit Values (TLVs) for nickel and all its compounds to 0.05 mg/m³. The TLV has been opposed by the NiDI and the NiPERA. A revision of the intended change has been proposed: 0.5 mg/m³ for nickel metal, 0.1 mg/m³ for insoluble nickel compounds, and 0.05 mg/m³ for soluble nickel compounds. (The intended TLV of 0.05 mg/m³ for the soluble nickel compounds is the same TLV for hexavalent chromium set in 1994.) The ACGIH has listed nickel oxides, subsulfides, and nickel carbonyl as confirmed human carcinogens. It is likely that the ACGIH will propose that nickel and all its compounds be classified as confirmed human carcinogens. (Crawford, 1996a) Both NiPERA and NiDI dispute the inclusion of the other nickel substances based on current evidence.

Nickel as an Alternative

The toxic effects of chromium coatings have caused a search for an alternative metal coating. A patented nickel-tungsten-silicon (Ni-W-SiC) composite electroplating process is being considered as an alternative to replace functional (hard) chromium coatings. Although the Ni-W-SiC process has several benefits, the primary concern is that, as a substitute, the nickel-tungsten process contains ingredients that have similar health and environmental concerns as chromium. The allergenic character and carcinogeneity of specific nickel compounds is noted in several studies. (Crawford, 1996a; Simon, 1994; Darby, et. al., 1978) In addition, the increased efficiency of the plating solution of the Ni-W-SiC process with regard to plating speed must be balanced with the fact that the solution produces a wastewater that requires treatment and that the solutions are subject to biological decomposition (USEPA, 1994). In fact, the real and alleged effects of nickel on the environment and human health have caused some surface finishers to search for alternatives to nickel plating (Simon, 1994).

Acknowledgments

Sierra Research would like to acknowledge the following companies, agencies, and associations who provided information and data for this project: Foss Plating Company; South Coast Air Quality Management District; Randy Solganik, Metal Finishing Association of Southern California, Inc.; and M. Dean High and Dennis Becvar, Pacific Environmental Services, Inc. This report was submitted in fulfillment of Contract No. 9-328, entitled "Characterization of Emissions from Nickel Plating," by Sierra Research, Inc., under the sponsorship of the California Air Resources Board. Work was completed as of June 21, 1999.

The SCAQMD also conducted a source test in September 1998 at a nickel plating operation at California Technical Plating Company. These tests resulted in a nickel emission factor of 0.251 mg/A-hr for nickel plating with air agitation, and 0.090 for nickel plating without air agitation (see Appendix I). The tests were conducted on a fully enclosed 3 ft. by 5 ft. nickel plating tank, which is smaller than typical nickel plating tanks. Concerns were raised by MFASC regarding the representativeness of this plating operation; however, subsequent testing by the SCAQMD at Foss Plating resulted in a similar nickel emission factor for plating operations with air agitation.

Finally, the SCAQMD has reported an emission factor for elemental nickel emissions from bright and semi-bright nickel plating of 7.20 x 10⁻⁸ lb/A-hr. (SCAQMD, 1996) Converting this value to milligrams/A-hr results in an emission factor of 0.0327 mg/A-hr. This SCAQMD factor is not based on test data, but rather is based on a CARB chrome plating emission factor (5.2 mg/A-hr) adjusted to account for differences in nickel plating tank solution concentrations and cathode efficiencies.

Two other source tests identified previously in Table 3 (California Fine Wire in 1995 and the 1996 Deutsch test) did not include process rate data and simply reported nickel emissions in units of pounds per hour. Therefore, these data are not useful for developing nickel emission factors. Table 7 compares the results of the referenced source tests and SCAQMD emission factors.

Table 7 Comparison of Reported Nickel Emissi	ion Factors
Emission Factor Source	Emission Factor (mg/A-hr)
Deutsch 1991 Uncontrolled (1996 EPA AP-42)	40.8
Deutsch 1991 Controlled (1991 Kleinfelder Report)	26.4
Kaynar 1998 Uncontrolled (1998 PES Report)	0.652
SCAQMD 1998 Foss Plating without Air Agitation	0.369
SCAQMD 1998 Cal Technical Plating w/Air Agitation	0.251
Dickson, et al, 1987, for Nickel "Strike"	0.225
SCAQMD 1998 Foss Plating with Air Agitation	0.214
Kaynar 1998 Controlled (1998 PES Report)	0.116
SCAQMD 1998 Cal Technical Plating w/o Air Agitation	0.090
Foss Plating 1998 with Air Agitation (1998 PES Report)	0.0496
SCAQMD Calculation based on Chrome Plating	0.0327
Foss Plating 1998 w/o Air Agitation (1998 PES Report)	0.0239

Abstract

A literature search and surveys were conducted to identify and collect all available nickel emissions testing reports or information for airborne nickel releases from nickel plating operations. A comprehensive literature search of several databases (listed in Appendix C) was conducted to identify and collect available emissions-related information for the nickel plating industry. A detailed bibliography provides references for the documents cited, as well as other documents reviewed. The literature search was supplemented with survey calls to nickel plating associations, nickel plating operators, and regulatory agencies (see Appendices A and B). In addition, calls were made to approximately 50 nickel plating firms or service agencies and governmental agencies for the most current information (see Appendix D). The literature search indicated that the majority of the emissions data available for nickel plating belongs to the nickel platers and the U.S. Environmental Protection Agency (EPA). Another source of data is the National Institute for Occupational Safety and Health (NIOSH); however, these data are limited in scope.

Developing Emissions Factors

In conversations with industry representatives,* suggestions were made as to the development of appropriate emissions factors based on the activity in the plating bath. Several factors were suggested: one emission factor that accounts for air agitation of the plating bath, which occurs at intervals during the nickel plating process; two emission factors for the plating process of electrolytic nickel plating depending on the type of plating solution; and a separate factor for electroless nickel processes.

<u>Factors Affecting Emissions</u> - Several factors are discussed in the literature as affecting emissions in nickel plating operations: the current density applied, the surface area of the part plated, the plate thickness, and plating time. Other factors are the type of part to be plated, the orientation of the part in the tank, the surface tension of the plating bath and the plating bath solution itself. In addition, for nickel plating tanks where agitation occurs, the agitation, whether mechanical or air, affects the emissions.

Plating Emissions Factors - A review of the available source test results and literature resulted in eight documents reporting nickel emission factors (see Table 3). However, only six of these reported emission factors are tied to nickel process rates. [Note: all units shown are as published, and for comparison purposes are converted to mg/A-hr.] The first emission factor was compiled from a 1987 report to USEPA. (Dickson et al, 1987) The emission factor was reported for nickel "strike" but is noted as being viable for nickel plating, where the source is the entire process of nickel electro-deposition. The 1987 report defines nickel "strike" as "an electrodeposition operation in which a very thin film of metal is plated into a base material to facilitate further plating with another metal or with the same metal." The emission factor value is reported as 2.25 x 10E-4 g/A-hr (0.225 mg/A-hr). USEPA converts this factor to units of lb/A-hr and reports it as 4.95 x 10E-7 lb/A-hr. (USEPA, 1990, p. 228)

The second emission factor was collected from a 1991 air toxics sampling report at Deutsch Engineered Connecting Devices. (Kleinfelder, 1991) The emission factor reported by EPA for this test is 0.63 grains/A-hr for uncontrolled nickel emissions. (USEPA, 1996, p. 12.20-17) This converts to 40.8 mg/A-hr. However, the 1991 Deutsch test actually included six sample runs (two separate tests) measuring nickel emissions upstream of a packed bed scrubber, and six sample runs (two separate tests) measuring nickel emissions downstream of a wet scrubber. The nickel emission factor reported by Kleinfelder for the Deutsch source test was 26.4 mg/A-hr for controlled nickel emissions.

A third nickel emission factor was identified from an April 1998 source test performed by PES at Kaynar Technologies in Fullerton, California. This test reported nickel emission factors of 0.652 mg/A-hr for uncontrolled nickel plating, and 0.116 mg/A-hr for controlled nickel emissions from a horizontal packed bed scrubber.

^{*} Conversations with Randy Solganik, Dean High and Tom Miles.

^{**} The equation used to generate equivalent units in milligrams/A-hr is (0.63 grains/A-hr x 64.8 mg/grain).

Characterization of Emissions from Nickel Plating

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<u>Polypropylene Balls</u> - Polypropylene balls are used in the plating baths, floating on the surface to reduce heat loss, evaporation, and misting. Their use is limited due to certain factors. For automatic operations, the effectiveness of the balls is reduced as the balls are sometimes dragged out by the plating racks. Their usefulness in reducing misting is also inhibited by the fact that the balls tend to be pushed away from the anodes and cathodes where the surface of the bath is agitated by gassing. Polypropylene balls are estimated to control plating emissions by 68 to 82%. (USEPA, 1993, p. 4-33)

Cost Analysis

EPA Data - The cost analysis reviewed for this study (USEPA, 1993) included cost information based on several model plants with hard and decorative chromium electroplating and chromic anodizing operations. The cost estimates were presented for each of the control options and capital and annualized costs were estimated. The cost information for new operations was obtained from several vendors, with each vendor quoting a cost estimate based on the parameters of each model plant. Capital costs for ventilation systems, including exhaust hoods and ductwork, were reported separately from the control device estimates. The installation of the ventilation systems was based on OSHA requirements for chromium emissions in the workplace.

For each piece of equipment for a new operation, a complete analysis was conducted. The capital costs included the purchase cost of the control device and auxiliaries, direct installations costs, indirect costs and startup costs. The annualized cost involved direct operating costs such as utilities, labor and materials, indirect operating costs, and capital recovery costs.

A cost analysis of retrofitting existing operations was also estimated for each piece of control equipment. Data from the vendors included retrofit costs such as the modification of equipment as well as the removal and disposal of any existing control device. The actual cost of retrofitting varied depending on the specific facility, the layout and the existing control equipment. A scaling factor of 20% of the installed capital costs of control for new facilities was used to estimate the retrofit capital costs for existing facilities. To cover the cost of disposal and transportation, 5% of the vendor estimate was included. The annualized retrofitting costs for some of the control equipment were higher than costs for new facilities due to the higher capital recovery costs and higher indirect costs. Table 5 summarizes the 1993 USEPA cost data.

Executive Summary

The purpose of the current study, "Characterization of Emissions from Nickel Plating," is to further address the quantity of emitted nickel and nickel compounds from plating operations; the characteristics inherent to nickel plating operations that result in emissions; and, most importantly, the potential nickel and nickel compound emissions from these operations. Emissions estimates available from electroplating sources have been reviewed, and the quality of the estimates and source test results has been assessed as part of this work. For this report, an extensive search was conducted of the technical literature and several data sources pertaining to airborne nickel emissions from plating operations to characterize the emissions from nickel plating operations. The magnitude of emission factors as well as the impact of process variables on emissions are reported, along with an assessment of the cost and efficacy of potential control measures.

Nickel is used in electroplating and electroforming processes for varying purposes from engineering to decorative applications. In engineering applications, the plating process upgrades inexpensive metals to improve resistance to wear, corrosion, abrasion, scaling, and fretting. In decorative metal finishing, nickel plating plus a topcoat of brass, silver, gold, and lacquers provides pleasing finishes and a high-performing, corrosion-resistant product.

Generally, the application of nickel has followed overall economic activity due to its wide use in various sectors. The nickel plating industry has grown at an average rate of four percent per year since 1985. The worldwide use of nickel metal for plating is now approximately 81,700 metric tons (180 million pounds) and will continue to grow with the expansion of the world economy. There are approximately 500 metal finishing shops in California.

In June 1991, the State of California Air Resources Board published a report to evaluate the public exposure to nickel in California. The report reviewed several factors with regard to nickel: estimated population, exposure, ambient and indoor concentrations, uses, sources, emissions, chemical properties, and atmospheric persistence. Nickel's identification as a toxic air contaminant was based on the above-mentioned report and a health assessment report.

The process of nickel plating involves an electrode to be plated (cathode), the dissolution of a second electrode (the anode), and an aqueous solution of nickel salts. A direct current is applied between the two electrodes immersed in the electrolyte. The flow of the current causes the nickel plating to occur at the cathode. With nickel salts dissolved in the water, the increasing current causes the positively charged nickel ions (Ni⁺⁺) to react with two electrons (2e-). Conversely, metallic nickel dissolves to form divalent ions

contaminated air to the exhaust hood. The air movement must occur in a uniform, horizontal movement across the tank at a rate sufficiently high to compensate for any air disturbances across the tank due to cross drafts. The makeup air supply is another factor affecting the ventilation. Replacing or offsetting the air exhausted from the building allows the exhaust systems to work without having an increase in static pressure due to the negative pressure or suction in the building. The volumetric flow of the makeup air is dependent on the layout and siting of heat sources and the physical layout of the building relative to the tank location. For the push-pull system, additional factors apply. The amount of push air supplied, the size of the exhaust hood installed, and the extent to which obstructions are present in the air stream path are all factors that affect the performance of the system.

Emission Control Techniques - Based on a review of the literature, controlling emissions from chromic acid mist resulting from the electroplating and anodizing operations can be accomplished using several proven control devices. Most frequently the mist is controlled using mist eliminators and wet scrubbers. The following discussion of control techniques of emission controls is based on USEPA (1993), except where noted otherwise.

Mist Eliminators - The mist eliminators collect the mist from the gas stream by using inertial impaction and direct interception. Inertial impaction collects the droplets as large particles that collide with a stationary surface. Direct interception utilizes a fluid layer on the collection surface that intercepts the flow of the mist particles. For both inertial impaction and direct interception, the collected droplets drain to the bottom of the collection device. Although operated as dry units, the devices are periodically flushed with water to keep the collection surfaces clean.

Chevron-blade mist eliminators work with a horizontal flow configuration of one or more sets of parallel, chevron-shaped blades. The control of the mist occurs by changing the direction of the flow of the gas four times for each blade. The droplets adhere to the surface of the blades due to the inertial force. Washing the blades periodically releases the built-up particles. To prevent the water droplets from being drawn through the stack, the fan must be turned off during the washing. As the blades are washed, the wash water is then drained to the plating tank or to a wastewater treatment system. The most common blade designs are overlapping and sinusoidal wave. The overlapping edges of the overlapping design and the catchments of the sinusoidal design serve as collection troughs for droplets and promote drainage of the droplets in the collection sump. The performance of the chevron-blade mist eliminators depends on the face velocity of the gas stream across the blades, the spacing between blades, the tightness of seals between the blades and the walls of the unit, and the frequency of washing the blades. Control device vendors estimate that removal efficiencies range from 80 to 90 percent. (USEPA, 1993, p. 4-12)

Mesh-pad mist eliminators consist of layers of interlocked filaments densely packed between two supporting grids. The multiple layers are compacted and connected by thin filaments. The mesh pads are designed with three layer patterns: (1) layers with a crimp in the same direction, (2) layers with a crimp in alternate directions, and (3) spiral-wound layers. For particles larger than 3 um (0.12 mil) moving with sufficient velocity, inertial

District (SCAQMD) to confirm the accuracy of the MFASC Foss Plating results. The SCAQMD test produced a nickel emission factor of 0.214 mg/A-hr for nickel plating operations using air agitation, which is about four times higher than the MFASC test results. However, the SCAQMD conducted only one test run under slightly different operating conditions than the MFASC test. Therefore, additional testing is recommended in order to identify a typical emission factor for nickel plating operations.

Based on the literature, several methods are available for the capture and control of nickel emissions during plating operations. As with most electroplating processes, local exhaust ventilation is the most common method used to capture the mist from nickel plating baths. Access to the plating tanks requires the use of equipment that does not restrict the plating activity. As such, canopy hoods and enclosures are generally not used. More common is the capture of nickel emissions using lateral (slot) and push-pull exhaust hoods.

The control cost analysis reviewed for this study (USEPA, 1993) included cost information based on several model plants with hard and decorative chromium electroplating and chromic anodizing operations. The cost estimates were presented for each of the control options and capital and annualized costs were estimated. The cost information for new operations was obtained from several vendors, with each vendor quoting a cost estimate based on the parameters of each model plant. Capital costs for ventilation systems, including exhaust hoods and ductwork, were reported separately from the control device estimates. The installation of the ventilation systems was based on OSHA requirements for chromium emissions in the workplace.

No information regarding nickel concentrations from plating operations at a facility's property line was located during the literature review. EPA's Industrial Source Complex (ISC3) and SCREEN3 Models are available to perform an ambient exposure assessment for emissions of nickel from nickel plating operations at the property line. The available data from several nickel plating operations indicate that, while some parts of the nickel plating operations exceed regulations, exposures generally are lower and in compliance with regulations overall. The only permissible exposure limit for nickel and any of its compounds is 1 mg/m³, except for nickel carbonyl.

The toxic effects of chromium coatings have caused a search for an alternative metal coating. A patented nickel-tungsten-silicon (Ni-W-SiC) composite electroplating process is being considered as an alternative to replace functional (hard) chromium coatings. Although the Ni-W-SiC process has several benefits, the primary concern is that, as a substitute, the nickel-tungsten process contains ingredients that have similar health and environmental concerns as chromium. In fact, the allergenic character and carcinogeneity of specific nickel compounds is noted in several studies. Furthermore, the real and alleged effects of nickel on the environment and human health have caused some surface finishers to search for alternatives to nickel plating.

source test. PES prepared a source test protocol that was reviewed and approved by ARB (see Appendix E for protocol and response to comments). Test results are summarized later in this section (see Table 6), and the source test report prepared by PES is included as Appendix F to this report.

The SCAQMD conducted a source test at the same Foss Plating facility in October 1998. This test was designed to address issues raised by the SCAQMD regarding high levels of background nickel and potential fugitive losses during the MFASC testing. The source test report prepared by the SCAQMD is included as Appendix H to this report.

The SCAQMD also conducted a source test at California Technical Plating in September 1998. MFASC expressed concerns that the plating tank used during this test was not representative of typical nickel plating operations. The SCAQMD's October test at Foss Plating was also meant to address validity concerns raised as a result of these September tests at California Technical Plating. A table summarizing the results of testing at California Technical Plating is included as Appendix I to this report.

Emission Capture Techniques - Based on the literature, several methods are available for the capture and control of nickel emissions during plating operations. As with most electroplating processes, local exhaust ventilation is the most common method used to capture the mist from nickel plating baths. Access to the plating tanks requires the use of equipment that does not restrict the plating activity. As such, canopy hoods and enclosures are generally not used. More common is the capture of nickel emissions using lateral (slot) and push-pull exhaust hoods. Where no drafts exist, the recommended capture air velocity across the liquid surface of the tank is 46 m/min (150 ft/min) for contaminants with high hazard potential and a high rate of mist evolution, such as chromic acid. (USEPA, 1993) The design ventilation rate depends on the hood type, the control velocity selected, and the width-to-length ratio of the tank. Table 4 lists the recommended ventilation rates for tanks with aspect ratios (width-to-length) less than 2.0 (USEPA, 1993, p. 4-3) If the aspect ratio exceeds 2.0, the option to ventilate parallel to the long dimension of the tank is not practicable. (USEPA, 1993, p. 4-2) Although the ventilation rates in Table 4 are the parameters for capturing chromic acid mist, calls made to the American Industrial Hygiene Association verified that "all other things being equal, the parameters should be about the same for ventilating nickel mist."

Correspondence with Heather D. Borman, Industrial Hygienist, State Compensation Insurance Fund, dated January 1, 1997.

1. Introduction

The literature documents the extensive use of nickel in electroplating and electroforming processes for many reasons. Used typically to improve substrate quality, nickel can be applied as an intermediate layer or as a part of any alloy deposition. Its use varies from engineering to decorative applications, due to several of its properties.

In engineering applications, the nickel coatings are used for their physical and mechanical properties. The plating process upgrades inexpensive metals to improve resistance to wear, corrosion, abrasion, scaling, and fretting. Nickel plating is applied to the surfaces of new and old parts, leaving a smooth, matte finish. The coating enhances the value of the equipment and parts in many industries: aeronautics, automotive, electronics, food processing, ship building, rubber manufacture, and others. Approximately 20% of nickel consumed in metal plating occurs for engineering and electroforming purposes. (DiBari, 1994)

The largest part of nickel consumption in nickel plating, 80%, takes place in the decorative process. (DiBari, 1994) In decorative metal finishing, nickel plating plus a topcoat of brass, silver, gold, and lacquers provides pleasing finishes with several uses. Decorative nickel combined with chromium produces a high-performing, corrosion-resistant product. Decorative plating has many applications in office equipment, jewelry, kitchen utensils, giftware, bathroom items, and more. The plating process produces deposits that are mirror-bright directly from the plating baths, with the majority requiring no mechanical finishing (bright nickel) or having deposits that are easily polished (semi-bright). (INCO, 1988)

Trends in Production

Industrial nickel plating technology began shortly after its discovery in 1842. The birth of the decorative process occurred less than 60 years ago when organic bright nickel plating was applied. Bright nickel plating was in high demand with the manufacture of automobiles and other products utilizing the mirror-bright deposits.

With the growth of the automobile industry, bright nickel plating grew rapidly after 1945. The failure of the single-layer bright nickel coatings led to industry-wide efforts to develop semi-bright nickel coatings and double and triple layer decorative coatings. Improvements in the techniques for plating on plastics and on aluminum alloys, in corrosion-testing techniques, and in methods of studying corrosion all led to the improved quality of electroplated nickel. The 1970s brought a decline in the use of nickel plating in

of acid misting from the plating baths is dependent mainly on the efficiencies of the baths. Nickel plating baths have high cathode efficiencies so that the generation of mist is minimal. (USEPA, 1993) Only about 3% of the electrical current releases hydrogen at the cathode, and practically no oxygen is emitted at the anodes during the process.

According to a study by USEPA (1984), the emissions from plating shops occur during the handling of nickel salts used to prepare the solutions, the plating process, and the grinding, polishing, and cutting operations performed on the finished product and scrap metal. As mentioned above, hydrogen and oxygen gases are generated from the nickel salts and emitted as a mist during the plating process. However, EPA states that nickel emissions from misting are generally very low or nonexistent due to the low temperature and low current densities used in the nickel plating baths. Based on the high cathode efficiencies (95 to 98%) and baths operated at moderate temperatures and low to moderate current densities, nickel plating solutions containing sulfate and/or chloride exhibit low gassing. Thus, the need for local exhaust ventilation may be minimal due to these conditions. (USEPA, 1993, p. 3-15) In three studies cited by USEPA (1984, p. 98), the nickel air emissions were reported as negligible. Even those emissions that occurred during the grinding, polishing, and cutting were determined to be insignificant.

Further, a NIOSH study (1984) of five nickel electroplating baths at four facilities found very low concentrations of airborne nickel around unventilated nickel plating baths. Three of the tanks contained Watts nickel baths and two tanks contained nickel sulfamate. The tanks ranged in size from 370 to 1,680 gallons and none were covered, contained floating plastic balls, or were air agitated. Four of the tanks were mechanically agitated by other means. Area indoor air sample results for all five tanks showed extremely low nickel levels. The highest measurable nickel exposure was $6\mu g/m^3$ and the highest measurable tank-area concentration for nickel was $7\mu g/m^3$. Eight of 10 personal samples and 39 of 42 area samples were below the limit of detection. NIOSH concluded that the nickel exposure from unventilated nickel sulfate (Watts bath) and nickel sulfamate tanks is not a problem. Increased temperature (up to 160°) did not result in high nickel levels, confirming that plating baths tested did not need exhaust ventilation.

Source Test Method - ARB uses its Method 433 source test procedure to determine if nickel compounds are present in the exhaust from plating operations. In Method 433, particulate and gaseous phase nickel compounds are withdrawn isokinetically from the stack using a sample train and collected on a glass fiber filter, or in impingers that contain nitric acid. The typical detection limit for ARB Method 433 is 40 ug/L of solution analyzed. For the solution analyzed, the impinger catch, and the weak acid extract used for sample recovery of the sampling train, a typical listed working range for the method is between 300 ug/L and 5,000 ug/L. However, it should be noted that using Method 433 and the minimum detection limit of 40 ug/L, it would take 714 minutes, or 30 hours, to test for 7 ug/m³ of nickel compounds in the air above an unventilated nickel tank, such as the measurement made by NIOSH that is described in the previous paragraph. For the measurement of nickel present at lower concentrations or nickel that is present with compounds that interfere with the absorption of nickel, ARB approves equivalent procedures on a case-by-case basis. These include furnace atomic absorption spectrometry, argon plasma atomic emission spectrometry, neutron activation analysis, and x-ray fluorescence. Based on telephone calls to local air districts in California, ARB

Additionally, Assembly Bill 2588, the Toxic "Hot Spots" Information and Assessment Act, was enacted by the California legislature in 1987. The intent of the Act was to gather information on substances (toxic air contaminants) that may pose a chronic or acute risk to public health when present in the ambient air. Further, this legislation requires industry to provide the information to the public regarding the emissions of toxic air contaminants and their impact on public health. To meet the requirements of the Act, the AB2588 program was implemented in four major stages: (1) local air districts and industry prepared an inventory of toxic compounds emitted by facility, (2) local air districts and ARB prioritized facilities for further scrutiny based on the facility emission of toxic compounds, (3) high priority facilities prepared a comprehensive health risk assessment, and (4) the health risk assessment results were made available to the public. Based on ARB's compilation of the data, 42 facilities estimated emissions from nickel plating operations under the AB2588 program (ARB ATEDS).

Description of Operations

General Features of Nickel Plating - Nickel plating produces coatings that are protective, bright, smooth, corrosion resistant, wear resistant, solderable, and magnetic. The nickel coating enhances the appearance, extends the life, and improves the performance of many products. For all the plating processes (decorative, engineering, and electroforming), certain features are common.

The Plating Process - For the deposition of a layer of nickel on a substrate, the process involves an electrode to be plated (cathode), the dissolution of a second electrode (the anode), and an aqueous solution of nickel salts. A direct current is applied between the two electrodes immersed in the electrolyte. The flow of the current causes the nickel plating to occur at the cathode. With nickel salts dissolved in the water, the increasing current causes the positively charged nickel ions (Ni⁺⁺) to react with two electrons (2e-). Conversely, metallic nickel dissolves to form divalent ions at the anode. The nickel ions formed at the anode constantly replenish the nickel ions discharged at the cathode. As such, the nickel plating operation continues uninterrupted for long periods of time.

The deposition of nickel (thickness) at the cathode is dependent on the current density (amperes) and the amount of time. A small percentage of the current used in nickel plating is consumed at the cathode in discharging hydrogen ions. Cathode efficiency values are between 93% and 97% for most nickel processes (DiBari, 1993; USEPA, 1993; SCAQMD, 1996) and have been quoted as being as high as 98% (Watson, 1989, p. 2) The exact value is dependent upon plating conditions such as pH, cathodic current, and additives used. These efficiency values must be considered when estimating the weight and thickness of the nickel. Table 1 lists the deposition rates for nickel at various current densities based on a 96.5% cathode efficiency, and includes values for coating thickness, weight per unit area, current density, and time of plating. (DiBari, 1993)

2. Materials and Methods

A literature search and surveys were conducted to identify and collect all available nickel emissions testing reports or information for airborne nickel releases from nickel plating operations. A comprehensive literature search of several databases (listed in Appendix C) was conducted to identify and collect available emissions-related information for the nickel plating industry. Section 4 lists references for the documents cited, as well as other documents reviewed. The literature search was supplemented with survey calls to nickel plating associations, nickel plating operators, and regulatory agencies (see Appendices A and B). In addition, calls were made to approximately 50 nickel plating firms or service agencies and governmental agencies for the most current information (see Appendix D).

The literature was reviewed to collect information on the control devices and ventilation methods used in the nickel plating operations. None of the literature encountered had data on existing control equipment or required control equipment for nickel plating operations. Exhaustive calls were made to several associations in the industry as well as to USEPA and NIOSH. None of the conversations were fruitful other than to reiterate the earlier finding that no studies had been done that included control equipment for nickel plating and, according to EPA, there are no requirements for control equipment for nickel plating operations. As a result, the bulk of the information on control equipment that follows is gleaned from work (USEPA, 1993) on chromium emissions resulting from chrome electroplating and anodizing operations. This EPA report most closely resembled the information needed for this study.

To supplement the EPA data, calls were made to different firms in the industry as well as to industry research agencies. As much as possible, questions were asked to carefully define those chromium emission control devices and emission capture techniques that were applicable to the nickel plating operations.

Additional testing is recommended to better characterize emissions from nickel plating operations. The best documented emissions data available were provided by the MFASC and the SCAQMD, each of which conducted emissions source tests at a nickel plating facility in Santa Fe Springs, California during 1998. The source testing firm hired by MFASC, Pacific Environmental Services, Inc., (PES) prepared a detailed source testing protocol for this test (see Appendix E). Results from the MFASC test are included as Appendix F. The results of the SCAQMD test are included as Appendix H.

							Table 2	e 2										
		Fypical	Compo	sitions,	Opera of De	ting Co	ndition rom Se	perating Conditions and Approximat of Deposits from Several Electrolytes	proxin ectroly(Typical Compositions, Operating Conditions and Approximate Mechanical Properties of Deposits from Several Electrolytes	hanical	Proper	ies			:		
Constituents	Chl	All Chloride	Chi	Chloride Sulfate	, - Fluo	All Fluoborate	A	All Sulfate	Sulf	All Sulfamate	Chk Sulfa	Chloride Sulfamate	H Sulf	Hard Sulfamate	W	Watts	Hard Watts	rd tts
					Туріса	l Electroly	te Compo	Typical Electrolyte Composition g / L (0z / gal)	/ L. (oz /	gal)								
Total Nickel	75	(10)	86.4	(11.5)	75	(10)	70	(6.3)	84	(11.2)	84	(11.2)	45	(9)	8/	(10.4)	09	(8)
Nickel Chloride	300	(40)	158	(21)							22.5	(3)	7.5	(1)	09	(8)	45	(9)
Nickel Sulfate			188	(25)			330	(44)							300	(40)	292	(35)
Nickel Sulfamate									450	(09)	428	(25)	248	(33)				
Nickel Fluoborate					300	(40)												
Boric Acid	30	(4)	37.5	(2)	30	(4)	30	(4)	37.5	(5)	37.5	(5)	30	(4)	30	(4)	30	(4)
Anti Pitter	×		×		Х				×		X		×				X	
Addition Agent													O _S Se	Optional Stress Reducer			Optional Stress Reducer	onal SS Icer
						Ō	rerating C	Operating Conditions										
Temperature °C (°F)	55	(130)	55	(130)	55	(130)	55	(130)	09	(140)	09	(140)	55	(130)	55	(130)	50	(122)
Hq	2.0		3.0		2.7		1.5		4.0		4.0		5.0		3.0		5.0	
Current Density, A/m³ (A/ft³)	540	(20)	540	(20)	320	(30)	400	(40)	540	(50)	540	(20)	009	(09)	540	(50)	540	(50)
						Me	chanical	Mechanical Properties										
Tensile Strength, MPa (ksi)	069	(100)	517	(75)	400	(85)	480	(70)	413	(09)	758	(110)	968	(130)	413	(09)	1170	(170)
Hardness, DPN (100 g toad)	240		230		150		170		061		300		470		150		350	
Elongation, % in 50.8 mm (2 inches)	14		20		30		28		30		5		9		28		2	
Internal Stress, MPa (ksi)	345	(50)	220	(32)	138	(20)	117	(11)	4	(2)	69	(10)	Var Acc to Ar	Variable According to Addition Agent	138	(20)	Variable According to Addition Agent	able ding lition ent

Source: DiBari, G. (1993). Nickel Plating. Metals Finishing Guidebook and Directory Issue, p. 233.

							Table 2	3.2										
	I	ypical	Сошро	sitions, (Operat of De	ting Cor posits fr	nditions om Sev	perating Conditions and Approximat of Deposits from Several Electrolytes	proxin	Typical Compositions, Operating Conditions and Approximate Mechanical Properties of Deposits from Several Electrolytes	nanical	Propert	ies					
Constituents	All Chłoride	II rride	Se Gir	Chloride Sulfate	A Fluot	All Fluoborate	All Sulfate	II ate	4 Sulfi	All Sulfamate	Chloride Sulfamate	ride mate	H. Sulf	Hard Sulfamate	Watts	ıtts	Hard Watts	d ts
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Anti Pitter	×		×		×				×		×		×				×	
Addition Agent													o o	Optional Stress Reducer			Optional Stress Reducer	onal SS
						7 8	grating C	Oversting Conditions										
Tonnarahure of (0E)	55	(130)	55	(130)	55	(130)	55	(130)	99	(140)	09	(140)	55	(130)	55	(130)	50	(122)
Hq	2.0		3.0		2.7		1.5		4.0		4.0		5.0		3.0		5.0	
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of acid misting from the plating baths is dependent mainly on the efficiencies of the baths. Nickel plating baths have high cathode efficiencies so that the generation of mist is minimal. (USEPA, 1993) Only about 3% of the electrical current releases hydrogen at the cathode, and practically no oxygen is emitted at the anodes during the process.

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1. Introduction

The literature documents the extensive use of nickel in electroplating and electroforming processes for many reasons. Used typically to improve substrate quality, nickel can be applied as an intermediate layer or as a part of any alloy deposition. Its use varies from engineering to decorative applications, due to several of its properties.

In engineering applications, the nickel coatings are used for their physical and mechanical properties. The plating process upgrades inexpensive metals to improve resistance to wear, corrosion, abrasion, scaling, and fretting. Nickel plating is applied to the surfaces of new and old parts, leaving a smooth, matte finish. The coating enhances the value of the equipment and parts in many industries: aeronautics, automotive, electronics, food processing, ship building, rubber manufacture, and others. Approximately 20% of nickel consumed in metal plating occurs for engineering and electroforming purposes. (DiBari, 1994)

The largest part of nickel consumption in nickel plating, 80%, takes place in the decorative process. (DiBari, 1994) In decorative metal finishing, nickel plating plus a topcoat of brass, silver, gold, and lacquers provides pleasing finishes with several uses. Decorative nickel combined with chromium produces a high-performing, corrosion-resistant product. Decorative plating has many applications in office equipment, jewelry, kitchen utensils, giftware, bathroom items, and more. The plating process produces deposits that are mirror-bright directly from the plating baths, with the majority requiring no mechanical finishing (bright nickel) or having deposits that are easily polished (semi-bright). (INCO, 1988)

Trends in Production

Industrial nickel plating technology began shortly after its discovery in 1842. The birth of the decorative process occurred less than 60 years ago when organic bright nickel plating was applied. Bright nickel plating was in high demand with the manufacture of automobiles and other products utilizing the mirror-bright deposits.

With the growth of the automobile industry, bright nickel plating grew rapidly after 1945. The failure of the single-layer bright nickel coatings led to industry-wide efforts to develop semi-bright nickel coatings and double and triple layer decorative coatings. Improvements in the techniques for plating on plastics and on aluminum alloys, in corrosion-testing techniques, and in methods of studying corrosion all led to the improved quality of electroplated nickel. The 1970s brought a decline in the use of nickel plating in

source test. PES prepared a source test protocol that was reviewed and approved by ARB (see Appendix E for protocol and response to comments). Test results are summarized later in this section (see Table 6), and the source test report prepared by PES is included as Appendix F to this report.

The SCAQMD conducted a source test at the same Foss Plating facility in October 1998. This test was designed to address issues raised by the SCAQMD regarding high levels of background nickel and potential fugitive losses during the MFASC testing. The source test report prepared by the SCAQMD is included as Appendix H to this report.

The SCAQMD also conducted a source test at California Technical Plating in September 1998. MFASC expressed concerns that the plating tank used during this test was not representative of typical nickel plating operations. The SCAQMD's October test at Foss Plating was also meant to address validity concerns raised as a result of these September tests at California Technical Plating. A table summarizing the results of testing at California Technical Plating is included as Appendix I to this report.

Emission Capture <u>Techniques</u> - Based on the literature, several methods are available for the capture and control of nickel emissions during plating operations. As with most electroplating processes, local exhaust ventilation is the most common method used to capture the mist from nickel plating baths. Access to the plating tanks requires the use of equipment that does not restrict the plating activity. As such, canopy hoods and enclosures are generally not used. More common is the capture of nickel emissions using lateral (slot) and push-pull exhaust hoods. Where no drafts exist, the recommended capture air velocity across the liquid surface of the tank is 46 m/min (150 ft/min) for contaminants with high hazard potential and a high rate of mist evolution, such as chromic acid. (USEPA, 1993) The design ventilation rate depends on the hood type, the control velocity selected, and the width-to-length ratio of the tank. Table 4 lists the recommended ventilation rates for tanks with aspect ratios (width-to-length) less than 2.0 (USEPA, 1993, p. 4-3) If the aspect ratio exceeds 2.0, the option to ventilate parallel to the long dimension of the tank is not practicable. (USEPA, 1993, p. 4-2) Although the ventilation rates in Table 4 are the parameters for capturing chromic acid mist, calls made to the American Industrial Hygiene Association verified that "all other things being equal, the parameters should be about the same for ventilating nickel mist."

^{*} Correspondence with Heather D. Borman, Industrial Hygienist, State Compensation Insurance Fund, dated January 1, 1997.

District (SCAQMD) to confirm the accuracy of the MFASC Foss Plating results. The SCAQMD test produced a nickel emission factor of 0.214 mg/A-hr for nickel plating operations using air agitation, which is about four times higher than the MFASC test results. However, the SCAQMD conducted only one test run under slightly different operating conditions than the MFASC test. Therefore, additional testing is recommended in order to identify a typical emission factor for nickel plating operations.

Based on the literature, several methods are available for the capture and control of nickel emissions during plating operations. As with most electroplating processes, local exhaust ventilation is the most common method used to capture the mist from nickel plating baths. Access to the plating tanks requires the use of equipment that does not restrict the plating activity. As such, canopy hoods and enclosures are generally not used. More common is the capture of nickel emissions using lateral (slot) and push-pull exhaust hoods.

The control cost analysis reviewed for this study (USEPA, 1993) included cost information based on several model plants with hard and decorative chromium electroplating and chromic anodizing operations. The cost estimates were presented for each of the control options and capital and annualized costs were estimated. The cost information for new operations was obtained from several vendors, with each vendor quoting a cost estimate based on the parameters of each model plant. Capital costs for ventilation systems, including exhaust hoods and ductwork, were reported separately from the control device estimates. The installation of the ventilation systems was based on OSHA requirements for chromium emissions in the workplace.

No information regarding nickel concentrations from plating operations at a facility's property line was located during the literature review. EPA's Industrial Source Complex (ISC3) and SCREEN3 Models are available to perform an ambient exposure assessment for emissions of nickel from nickel plating operations at the property line. The available data from several nickel plating operations indicate that, while some parts of the nickel plating operations exceed regulations, exposures generally are lower and in compliance with regulations overall. The only permissible exposure limit for nickel and any of its compounds is 1 mg/m³, except for nickel carbonyl.

The toxic effects of chromium coatings have caused a search for an alternative metal coating. A patented nickel-tungsten-silicon (Ni-W-SiC) composite electroplating process is being considered as an alternative to replace functional (hard) chromium coatings. Although the Ni-W-SiC process has several benefits, the primary concern is that, as a substitute, the nickel-tungsten process contains ingredients that have similar health and environmental concerns as chromium. In fact, the allergenic character and carcinogeneity of specific nickel compounds is noted in several studies. Furthermore, the real and alleged effects of nickel on the environment and human health have caused some surface finishers to search for alternatives to nickel plating.

contaminated air to the exhaust hood. The air movement must occur in a uniform, horizontal movement across the tank at a rate sufficiently high to compensate for any air disturbances across the tank due to cross drafts. The makeup air supply is another factor affecting the ventilation. Replacing or offsetting the air exhausted from the building allows the exhaust systems to work without having an increase in static pressure due to the negative pressure or suction in the building. The volumetric flow of the makeup air is dependent on the layout and siting of heat sources and the physical layout of the building relative to the tank location. For the push-pull system, additional factors apply. The amount of push air supplied, the size of the exhaust hood installed, and the extent to which obstructions are present in the air stream path are all factors that affect the performance of the system.

Emission Control Techniques - Based on a review of the literature, controlling emissions from chromic acid mist resulting from the electroplating and anodizing operations can be accomplished using several proven control devices. Most frequently the mist is controlled using mist eliminators and wet scrubbers. The following discussion of control techniques of emission controls is based on USEPA (1993), except where noted otherwise.

Mist Eliminators - The mist eliminators collect the mist from the gas stream by using inertial impaction and direct interception. Inertial impaction collects the droplets as large particles that collide with a stationary surface. Direct interception utilizes a fluid layer on the collection surface that intercepts the flow of the mist particles. For both inertial impaction and direct interception, the collected droplets drain to the bottom of the collection device. Although operated as dry units, the devices are periodically flushed with water to keep the collection surfaces clean.

Chevron-blade mist eliminators work with a horizontal flow configuration of one or more sets of parallel, chevron-shaped blades. The control of the mist occurs by changing the direction of the flow of the gas four times for each blade. The droplets adhere to the surface of the blades due to the inertial force. Washing the blades periodically releases the built-up particles. To prevent the water droplets from being drawn through the stack, the fan must be turned off during the washing. As the blades are washed, the wash water is then drained to the plating tank or to a wastewater treatment system. The most common blade designs are overlapping and sinusoidal wave. The overlapping edges of the overlapping design and the catchments of the sinusoidal design serve as collection troughs for droplets and promote drainage of the droplets in the collection sump. The performance of the chevron-blade mist eliminators depends on the face velocity of the gas stream across the blades, the spacing between blades, the tightness of seals between the blades and the walls of the unit, and the frequency of washing the blades. Control device vendors estimate that removal efficiencies range from 80 to 90 percent. (USEPA, 1993, p. 4-12)

Mesh-pad mist eliminators consist of layers of interlocked filaments densely packed between two supporting grids. The multiple layers are compacted and connected by thin filaments. The mesh pads are designed with three layer patterns: (1) layers with a crimp in the same direction, (2) layers with a crimp in alternate directions, and (3) spiral-wound layers. For particles larger than 3 um (0.12 mil) moving with sufficient velocity, inertial

Executive Summary

The purpose of the current study, "Characterization of Emissions from Nickel Plating," is to further address the quantity of emitted nickel and nickel compounds from plating operations; the characteristics inherent to nickel plating operations that result in emissions; and, most importantly, the potential nickel and nickel compound emissions from these operations. Emissions estimates available from electroplating sources have been reviewed, and the quality of the estimates and source test results has been assessed as part of this work. For this report, an extensive search was conducted of the technical literature and several data sources pertaining to airborne nickel emissions from plating operations to characterize the emissions from nickel plating operations. The magnitude of emission factors as well as the impact of process variables on emissions are reported, along with an assessment of the cost and efficacy of potential control measures.

Nickel is used in electroplating and electroforming processes for varying purposes from engineering to decorative applications. In engineering applications, the plating process upgrades inexpensive metals to improve resistance to wear, corrosion, abrasion, scaling, and fretting. In decorative metal finishing, nickel plating plus a topcoat of brass, silver, gold, and lacquers provides pleasing finishes and a high-performing, corrosion-resistant product.

Generally, the application of nickel has followed overall economic activity due to its wide use in various sectors. The nickel plating industry has grown at an average rate of four percent per year since 1985. The worldwide use of nickel metal for plating is now approximately 81,700 metric tons (180 million pounds) and will continue to grow with the expansion of the world economy. There are approximately 500 metal finishing shops in California.

In June 1991, the State of California Air Resources Board published a report to evaluate the public exposure to nickel in California. The report reviewed several factors with regard to nickel: estimated population, exposure, ambient and indoor concentrations, uses, sources, emissions, chemical properties, and atmospheric persistence. Nickel's identification as a toxic air contaminant was based on the above-mentioned report and a health assessment report.

The process of nickel plating involves an electrode to be plated (cathode), the dissolution of a second electrode (the anode), and an aqueous solution of nickel salts. A direct current is applied between the two electrodes immersed in the electrolyte. The flow of the current causes the nickel plating to occur at the cathode. With nickel salts dissolved in the water, the increasing current causes the positively charged nickel ions (Ni⁺⁺) to react with two electrons (2e-). Conversely, metallic nickel dissolves to form divalent ions

<u>Polypropylene Balls</u> - Polypropylene balls are used in the plating baths, floating on the surface to reduce heat loss, evaporation, and misting. Their use is limited due to certain factors. For automatic operations, the effectiveness of the balls is reduced as the balls are sometimes dragged out by the plating racks. Their usefulness in reducing misting is also inhibited by the fact that the balls tend to be pushed away from the anodes and cathodes where the surface of the bath is agitated by gassing. Polypropylene balls are estimated to control plating emissions by 68 to 82%. (USEPA, 1993, p. 4-33)

Cost Analysis

EPA Data - The cost analysis reviewed for this study (USEPA, 1993) included cost information based on several model plants with hard and decorative chromium electroplating and chromic anodizing operations. The cost estimates were presented for each of the control options and capital and annualized costs were estimated. The cost information for new operations was obtained from several vendors, with each vendor quoting a cost estimate based on the parameters of each model plant. Capital costs for ventilation systems, including exhaust hoods and ductwork, were reported separately from the control device estimates. The installation of the ventilation systems was based on OSHA requirements for chromium emissions in the workplace.

For each piece of equipment for a new operation, a complete analysis was conducted. The capital costs included the purchase cost of the control device and auxiliaries, direct installations costs, indirect costs and startup costs. The annualized cost involved direct operating costs such as utilities, labor and materials, indirect operating costs, and capital recovery costs.

A cost analysis of retrofitting existing operations was also estimated for each piece of control equipment. Data from the vendors included retrofit costs such as the modification of equipment as well as the removal and disposal of any existing control device. The actual cost of retrofitting varied depending on the specific facility, the layout and the existing control equipment. A scaling factor of 20% of the installed capital costs of control for new facilities was used to estimate the retrofit capital costs for existing facilities. To cover the cost of disposal and transportation, 5% of the vendor estimate was included. The annualized retrofitting costs for some of the control equipment were higher than costs for new facilities due to the higher capital recovery costs and higher indirect costs. Table 5 summarizes the 1993 USEPA cost data.

Characterization of Emissions from Nickel Plating

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Developing Emissions Factors

In conversations with industry representatives,* suggestions were made as to the development of appropriate emissions factors based on the activity in the plating bath. Several factors were suggested: one emission factor that accounts for air agitation of the plating bath, which occurs at intervals during the nickel plating process; two emission factors for the plating process of electrolytic nickel plating depending on the type of plating solution; and a separate factor for electroless nickel processes.

<u>Factors Affecting Emissions</u> - Several factors are discussed in the literature as affecting emissions in nickel plating operations: the current density applied, the surface area of the part plated, the plate thickness, and plating time. Other factors are the type of part to be plated, the orientation of the part in the tank, the surface tension of the plating bath and the plating bath solution itself. In addition, for nickel plating tanks where agitation occurs, the agitation, whether mechanical or air, affects the emissions.

Plating Emissions Factors - A review of the available source test results and literature resulted in eight documents reporting nickel emission factors (see Table 3). However, only six of these reported emission factors are tied to nickel process rates. [Note: all units shown are as published, and for comparison purposes are converted to mg/A-hr.] The first emission factor was compiled from a 1987 report to USEPA. (Dickson et al, 1987) The emission factor was reported for nickel "strike" but is noted as being viable for nickel plating, where the source is the entire process of nickel electro-deposition. The 1987 report defines nickel "strike" as "an electrodeposition operation in which a very thin film of metal is plated into a base material to facilitate further plating with another metal or with the same metal." The emission factor value is reported as 2.25 x 10E-4 g/A-hr (0.225 mg/A-hr). USEPA converts this factor to units of lb/A-hr and reports it as 4.95 x 10E-7 lb/A-hr. (USEPA, 1990, p. 228)

The second emission factor was collected from a 1991 air toxics sampling report at Deutsch Engineered Connecting Devices. (Kleinfelder, 1991) The emission factor reported by EPA for this test is 0.63 grains/A-hr for uncontrolled nickel emissions. (USEPA, 1996, p. 12.20-17) This converts to 40.8 mg/A-hr. However, the 1991 Deutsch test actually included six sample runs (two separate tests) measuring nickel emissions upstream of a packed bed scrubber, and six sample runs (two separate tests) measuring nickel emissions downstream of a wet scrubber. The nickel emission factor reported by Kleinfelder for the Deutsch source test was 26.4 mg/A-hr for controlled nickel emissions.

A third nickel emission factor was identified from an April 1998 source test performed by PES at Kaynar Technologies in Fullerton, California. This test reported nickel emission factors of 0.652 mg/A-hr for uncontrolled nickel plating, and 0.116 mg/A-hr for controlled nickel emissions from a horizontal packed bed scrubber.

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^{*} Conversations with Randy Solganik, Dean High and Tom Miles.

The equation used to generate equivalent units in milligrams/A-hr is (0.63 grains/A-hr x 64.8 mg/grain).

Abstract

A literature search and surveys were conducted to identify and collect all available nickel emissions testing reports or information for airborne nickel releases from nickel plating operations. A comprehensive literature search of several databases (listed in Appendix C) was conducted to identify and collect available emissions-related information for the nickel plating industry. A detailed bibliography provides references for the documents cited, as well as other documents reviewed. The literature search was supplemented with survey calls to nickel plating associations, nickel plating operators, and regulatory agencies (see Appendices A and B). In addition, calls were made to approximately 50 nickel plating firms or service agencies and governmental agencies for the most current information (see Appendix D). The literature search indicated that the majority of the emissions data available for nickel plating belongs to the nickel platers and the U.S. Environmental Protection Agency (EPA). Another source of data is the National Institute for Occupational Safety and Health (NIOSH); however, these data are limited in scope.

The SCAQMD also conducted a source test in September 1998 at a nickel plating operation at California Technical Plating Company. These tests resulted in a nickel emission factor of 0.251 mg/A-hr for nickel plating with air agitation, and 0.090 for nickel plating without air agitation (see Appendix I). The tests were conducted on a fully enclosed 3 ft. by 5 ft. nickel plating tank, which is smaller than typical nickel plating tanks. Concerns were raised by MFASC regarding the representativeness of this plating operation; however, subsequent testing by the SCAQMD at Foss Plating resulted in a similar nickel emission factor for plating operations with air agitation.

Finally, the SCAQMD has reported an emission factor for elemental nickel emissions from bright and semi-bright nickel plating of 7.20 x 10⁻⁸ lb/A-hr. (SCAQMD, 1996) Converting this value to milligrams/A-hr results in an emission factor of 0.0327 mg/A-hr. This SCAQMD factor is not based on test data, but rather is based on a CARB chrome plating emission factor (5.2 mg/A-hr) adjusted to account for differences in nickel plating tank solution concentrations and cathode efficiencies.

Two other source tests identified previously in Table 3 (California Fine Wire in 1995 and the 1996 Deutsch test) did not include process rate data and simply reported nickel emissions in units of pounds per hour. Therefore, these data are not useful for developing nickel emission factors. Table 7 compares the results of the referenced source tests and SCAQMD emission factors.

Table 7 Comparison of Reported Nickel Emission Factors						
Emission Factor Source Emission Factor						
Deutsch 1991 Uncontrolled (1996 EPA AP-42)	40.8					
Deutsch 1991 Controlled (1991 Kleinfelder Report)	26.4					
Kaynar 1998 Uncontrolled (1998 PES Report)	0.652					
SCAQMD 1998 Foss Plating without Air Agitation	0.369					
SCAQMD 1998 Cal Technical Plating w/Air Agitation	0.251					
Dickson, et al, 1987, for Nickel "Strike"	0.225					
SCAQMD 1998 Foss Plating with Air Agitation	0.214					
Kaynar 1998 Controlled (1998 PES Report)	0.116					
SCAQMD 1998 Cal Technical Plating w/o Air Agitation	0.090					
Foss Plating 1998 with Air Agitation (1998 PES Report)	0.0496					
SCAQMD Calculation based on Chrome Plating	0.0327					
Foss Plating 1998 w/o Air Agitation (1998 PES Report)	0.0239					

Acknowledgments

Sierra Research would like to acknowledge the following companies, agencies, and associations who provided information and data for this project: Foss Plating Company; South Coast Air Quality Management District; Randy Solganik, Metal Finishing Association of Southern California, Inc.; and M. Dean High and Dennis Becvar, Pacific Environmental Services, Inc. This report was submitted in fulfillment of Contract No. 9-328, entitled "Characterization of Emissions from Nickel Plating," by Sierra Research, Inc., under the sponsorship of the California Air Resources Board. Work was completed as of June 21, 1999.

Workplace exposure data were located. According to a study by Crawford (1996a), nickel exposures in the workplace are unknown due to a lack of resources to measure exposure. However, notes Crawford, data from various nickel plating operations are detailed in a health guide published jointly by the Nickel Producers Environmental Research Association (NiPERA) and the Nickel Development Institute (NiDI) (1994). The available data from several nickel plating operations indicate that, while some parts of the nickel plating operations exceed regulations, exposures generally are lower and in compliance with regulations overall. (Crawford, 1996a, p. 66)

Exposure Limits - The permissible exposure limits are different, though similar, from one country to the next. For the United States, the limits set by OSHA are 1 mg/m³ for nickel metal and insoluble nickel compounds and 0.1 mg/m³ for soluble compounds. However, the 0.1 mg/m³ value was rescinded because it had been improperly established. As a result, the only permissible exposure limit for nickel and any of its compounds, except for nickel carbonyl, is 1 mg/m³. (Crawford, 1996a)

The American Conference of Governmental Industrial Hygienists (ACGIH) has put nickel soluble compounds on the "Notice of Intended Changes List for 1996." The intended change was to lower the Threshold Limit Values (TLVs) for nickel and all its compounds to 0.05 mg/m³. The TLV has been opposed by the NiDI and the NiPERA. A revision of the intended change has been proposed: 0.5 mg/m³ for nickel metal, 0.1 mg/m³ for insoluble nickel compounds, and 0.05 mg/m³ for soluble nickel compounds is the same TLV for hexavalent chromium set in 1994.) The ACGIH has listed nickel oxides, subsulfides, and nickel carbonyl as confirmed human carcinogens. It is likely that the ACGIH will propose that nickel and all its compounds be classified as confirmed human carcinogens. (Crawford, 1996a) Both NiPERA and NiDI dispute the inclusion of the other nickel substances based on current evidence.

Nickel as an Alternative

The toxic effects of chromium coatings have caused a search for an alternative metal coating. A patented nickel-tungsten-silicon (Ni-W-SiC) composite electroplating process is being considered as an alternative to replace functional (hard) chromium coatings. Although the Ni-W-SiC process has several benefits, the primary concern is that, as a substitute, the nickel-tungsten process contains ingredients that have similar health and environmental concerns as chromium. The allergenic character and carcinogeneity of specific nickel compounds is noted in several studies. (Crawford, 1996a; Simon, 1994; Darby, et. al., 1978) In addition, the increased efficiency of the plating solution of the Ni-W-SiC process with regard to plating speed must be balanced with the fact that the solution produces a wastewater that requires treatment and that the solutions are subject to biological decomposition (USEPA, 1994). In fact, the real and alleged effects of nickel on the environment and human health have caused some surface finishers to search for alternatives to nickel plating (Simon, 1994).

DISCLAMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

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CHARACTERIZATION OF EMISSIONS FROM NICKEL PLATING

VOLUME I – TECHNICAL REPORT

FINAL REPORT CONTRACT NO. 95-328

PREPARED FOR:

CALIFORNIA AIR RESOURCES BOARD
RESEARCH DIVISION
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Characterization of Emissions from Nickel Planting

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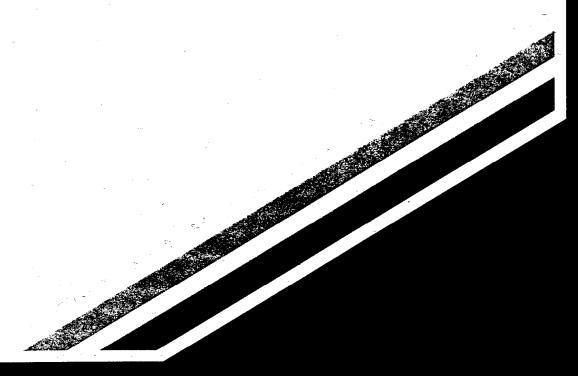
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The process of nickel plating involves an electrode to be plated (cathode), the dissolution of a second electrode (the anode), and an aqueous solution of nickel salts. A direct current is applied between the two electrodes immersed in the electrolyte. The flow of the current causes the nickel plating to occur at the cathode. With nickel salts dissolved in the water, the increasing current causes the positively charged nickel ions (Ni⁺⁺) to react with two electrons (2e-). Conversely, metallic nickel dissolves to form divalent ions

at the anode. The nickel ions formed at the anode constantly replenish the nickel ions discharged at the cathode.

The most commonly used nickel plating solutions are based on a mixture of nickel sulfate, nickel chloride and boric acid (Watts solution), and a sulfamate solution. The Watts solution is a simple and inexpensive plating bath that is easy to control and keep free from impurities. The sulfamate solutions, however, have certain advantages that make them extremely popular for electroforming. Nickel sulfamate solutions generate deposits that are low in stress, with high rates of deposition and high rates of thickness.

Mists are generated as a result of the plating process as hydrogen and oxygen gas evolve. The gas bubbles rise to the surface and may carry considerable liquid with them in the form of a fine mist. The release of gas is a function of the chemical or electrochemical activity in the tank. The rate of gassing depends on the activity in the tank, the strength and temperature of the solution, and the current densities in the tank. Nickel plating baths have high cathode efficiencies so that the generation of mist is minimal.

The emissions from plating shops occur during the handling of nickel salts used to prepare the solutions, the plating process, and the grinding, polishing, and cutting operations performed on the finished product and scrap metal. As mentioned above, hydrogen and oxygen gases are generated from the nickel salts and emitted as a mist during the plating process. However, nickel emissions from misting are generally very low due to the low temperature and low current densities used in the nickel plating baths.

Several factors are discussed in the literature as affecting emissions in nickel plating operations: the current density applied, the surface area of the part plated, the plate thickness and plating time. Other factors are the type of part to be plated, the orientation of the part in the tank, the surface tension of the plating bath, and the plating bath solution itself. In addition, for nickel plating tanks where agitation occurs, the agitation, whether mechanical or air, affects the emissions.

ARB uses its Method 433 source test procedure to determine if nickel compounds are present in the exhaust from plating operations. In Method 433, particulate and gaseous phase nickel compounds are withdrawn isokinetically from the stack using a sample train and collected on a glass fiber filter, or in impingers that contain nitric acid. The typical detection limit for ARB Method 433 is 40 ug/L of solution analyzed. For the measurement of nickel present at lower concentrations or nickel that is present with compounds that interfere with the absorption of nickel, ARB approves equivalent procedures on a case-by-case basis.

The literature review revealed a scarcity of source test data for nickel plating operations. Due to the lack of source test data, and as part of its industry effort to work with ARB, the Metal Finishing Association of Southern California (MFASC) conducted a source test at Foss Plating, a nickel plating facility in Santa Fe Springs, California, during April and May of 1998. Results of this test indicate that typical uncontrolled nickel plating operations using air agitation emit 0.0496 mg/amp-hr nickel. However, this test may have been confounded by high background levels of nickel, and additional testing was performed at the site during October 1998 by the South Coast Air Quality Management

District (SCAQMD) to confirm the accuracy of the MFASC Foss Plating results. The SCAQMD test produced a nickel emission factor of 0.214 mg/A-hr for nickel plating operations using air agitation, which is about four times higher than the MFASC test results. However, the SCAQMD conducted only one test run under slightly different operating conditions than the MFASC test. Therefore, additional testing is recommended in order to identify a typical emission factor for nickel plating operations.

Based on the literature, several methods are available for the capture and control of nickel emissions during plating operations. As with most electroplating processes, local exhaust ventilation is the most common method used to capture the mist from nickel plating baths. Access to the plating tanks requires the use of equipment that does not restrict the plating activity. As such, canopy hoods and enclosures are generally not used. More common is the capture of nickel emissions using lateral (slot) and push-pull exhaust hoods.

The control cost analysis reviewed for this study (USEPA, 1993) included cost information based on several model plants with hard and decorative chromium electroplating and chromic anodizing operations. The cost estimates were presented for each of the control options and capital and annualized costs were estimated. The cost information for new operations was obtained from several vendors, with each vendor quoting a cost estimate based on the parameters of each model plant. Capital costs for ventilation systems, including exhaust hoods and ductwork, were reported separately from the control device estimates. The installation of the ventilation systems was based on OSHA requirements for chromium emissions in the workplace.

No information regarding nickel concentrations from plating operations at a facility's property line was located during the literature review. EPA's Industrial Source Complex (ISC3) and SCREEN3 Models are available to perform an ambient exposure assessment for emissions of nickel from nickel plating operations at the property line. The available data from several nickel plating operations indicate that, while some parts of the nickel plating operations exceed regulations, exposures generally are lower and in compliance with regulations overall. The only permissible exposure limit for nickel and any of its compounds is 1 mg/m³, except for nickel carbonyl.

The toxic effects of chromium coatings have caused a search for an alternative metal coating. A patented nickel-tungsten-silicon (Ni-W-SiC) composite electroplating process is being considered as an alternative to replace functional (hard) chromium coatings. Although the Ni-W-SiC process has several benefits, the primary concern is that, as a substitute, the nickel-tungsten process contains ingredients that have similar health and environmental concerns as chromium. In fact, the allergenic character and carcinogeneity of specific nickel compounds is noted in several studies. Furthermore, the real and alleged effects of nickel on the environment and human health have caused some surface finishers to search for alternatives to nickel plating.

1. Introduction

The literature documents the extensive use of nickel in electroplating and electroforming processes for many reasons. Used typically to improve substrate quality, nickel can be applied as an intermediate layer or as a part of any alloy deposition. Its use varies from engineering to decorative applications, due to several of its properties.

In engineering applications, the nickel coatings are used for their physical and mechanical properties. The plating process upgrades inexpensive metals to improve resistance to wear, corrosion, abrasion, scaling, and fretting. Nickel plating is applied to the surfaces of new and old parts, leaving a smooth, matte finish. The coating enhances the value of the equipment and parts in many industries: aeronautics, automotive, electronics, food processing, ship building, rubber manufacture, and others. Approximately 20% of nickel consumed in metal plating occurs for engineering and electroforming purposes. (DiBari, 1994)

The largest part of nickel consumption in nickel plating, 80%, takes place in the decorative process. (DiBari, 1994) In decorative metal finishing, nickel plating plus a topcoat of brass, silver, gold, and lacquers provides pleasing finishes with several uses. Decorative nickel combined with chromium produces a high-performing, corrosion-resistant product. Decorative plating has many applications in office equipment, jewelry, kitchen utensils, giftware, bathroom items, and more. The plating process produces deposits that are mirror-bright directly from the plating baths, with the majority requiring no mechanical finishing (bright nickel) or having deposits that are easily polished (semi-bright). (INCO, 1988)

Trends in Production

Industrial nickel plating technology began shortly after its discovery in 1842. The birth of the decorative process occurred less than 60 years ago when organic bright nickel plating was applied. Bright nickel plating was in high demand with the manufacture of automobiles and other products utilizing the mirror-bright deposits.

With the growth of the automobile industry, bright nickel plating grew rapidly after 1945. The failure of the single-layer bright nickel coatings led to industry-wide efforts to develop semi-bright nickel coatings and double and triple layer decorative coatings. Improvements in the techniques for plating on plastics and on aluminum alloys, in corrosion-testing techniques, and in methods of studying corrosion all led to the improved quality of electroplated nickel. The 1970s brought a decline in the use of nickel plating in

the auto industry, however, with the increased use of urethane and other low-density materials replacing nickel-plated bumpers.

Generally, the application of nickel has followed overall economic activity due to its wide use in various sectors. The nickel plating industry has grown at an average rate of four percent per year since 1985. The worldwide use of nickel metal for plating is now approximately 81,700 metric tons (180 million pounds) and will continue to grow with the expansion of the world economy. (DiBari, 1994) The increased application of nickel has been the greatest in Japan, Taiwan, China, and other Asian countries. The market for nickel plating in the United States has been stable, with changes possibly occurring if the decline in automotive decorative plating reverses itself. The use of nickel plating in the automotive industry has bottomed out and may be reversing itself according to some experts. (DiBari, 1996) The increased popularity of vehicles using decorative nickel-plated hardware is the main reason for a potential upward trend in this market. For example, worldwide growth in the production of decorative plated styled wheels, plans for a new bumper plating plant, and expansion of existing automotive plating plants in the United States and Canada are all indications that the downward trend may be reversing itself.

The Regional Job Shop Directory located on the Internet (posted by Industry On Line, Inc.) indicates that there are approximately 500 metal finishing shops in California. Unfortunately, the directory does not separate the shops by type of metal plated.

History of Nickel Regulation

In June 1991, the State of California Air Resources Board published a report to evaluate the public exposure to nickel in California. The report reviewed several factors with regard to nickel: estimated population, exposure, ambient and indoor concentrations, uses, sources, emissions, chemical properties, and atmospheric persistence. Nickel's identification as a toxic air contaminant was based on the above-mentioned report and a health assessment report (Part B).

The purpose of the current study, "Characterization of Emissions from Nickel Plating," is to further address the quantity of emitted nickel and nickel compounds from plating operations; the characteristics inherent to nickel plating operations that result in emissions; and, most importantly, the potential nickel and nickel compound emissions from these operations. Emissions estimates available from electroplating sources have been reviewed, and the quality of the estimates and source test results have been assessed as part of this work. For this report, an extensive search was conducted of the technical literature and several data sources pertaining to airborne nickel emissions from plating operations to characterize the emissions from nickel plating operations. The magnitude of emission factors as well as the impact of process variables on emissions are reported along with an assessment of the cost and efficacy of potential control measures. Additional source testing is recommended to improve the quality and accuracy of the available emission factors for nickel plating.

Additionally, Assembly Bill 2588, the Toxic "Hot Spots" Information and Assessment Act, was enacted by the California legislature in 1987. The intent of the Act was to gather information on substances (toxic air contaminants) that may pose a chronic or acute risk to public health when present in the ambient air. Further, this legislation requires industry to provide the information to the public regarding the emissions of toxic air contaminants and their impact on public health. To meet the requirements of the Act, the AB2588 program was implemented in four major stages: (1) local air districts and industry prepared an inventory of toxic compounds emitted by facility, (2) local air districts and ARB prioritized facilities for further scrutiny based on the facility emission of toxic compounds, (3) high priority facilities prepared a comprehensive health risk assessment, and (4) the health risk assessment results were made available to the public. Based on ARB's compilation of the data, 42 facilities estimated emissions from nickel plating operations under the AB2588 program (ARB ATEDS).

Description of Operations

General Features of Nickel Plating - Nickel plating produces coatings that are protective, bright, smooth, corrosion resistant, wear resistant, solderable, and magnetic. The nickel coating enhances the appearance, extends the life, and improves the performance of many products. For all the plating processes (decorative, engineering, and electroforming), certain features are common.

The Plating Process - For the deposition of a layer of nickel on a substrate, the process involves an electrode to be plated (cathode), the dissolution of a second electrode (the anode), and an aqueous solution of nickel salts. A direct current is applied between the two electrodes immersed in the electrolyte. The flow of the current causes the nickel plating to occur at the cathode. With nickel salts dissolved in the water, the increasing current causes the positively charged nickel ions (Ni⁺⁺) to react with two electrons (2e-). Conversely, metallic nickel dissolves to form divalent ions at the anode. The nickel ions formed at the anode constantly replenish the nickel ions discharged at the cathode. As such, the nickel plating operation continues uninterrupted for long periods of time.

The deposition of nickel (thickness) at the cathode is dependent on the current density (amperes) and the amount of time. A small percentage of the current used in nickel plating is consumed at the cathode in discharging hydrogen ions. Cathode efficiency values are between 93% and 97% for most nickel processes (DiBari, 1993; USEPA, 1993; SCAQMD, 1996) and have been quoted as being as high as 98% (Watson, 1989, p. 2) The exact value is dependent upon plating conditions such as pH, cathodic current, and additives used. These efficiency values must be considered when estimating the weight and thickness of the nickel. Table 1 lists the deposition rates for nickel at various current densities based on a 96.5% cathode efficiency, and includes values for coating thickness, weight per unit area, current density, and time of plating. (DiBari, 1993)

Table 1 Data Sheet on Depositing Nickel (Based on 96.5% Cathode Efficiency)								
Minutes for Obtaining Coating at Various Current Densities (A/ft²)								
Thickness in Inches	Thickness in Micrometers	Oz / ft²	G/ft²	Amp-hr	10	20	50	100
0.0001	2.5	0.0721	2.04	1.9	12	6	2.4	1.2
0.0002	5.1	0.144	4.08	3.98	24	12	4.8	2.4
0.0005	12.7	0.360	10.20	9.95	59.6	30	12.2	6.1
0.0008	20.3	0.578	16.32	15.9	95.6	47.8	19.2	9.6
0.0010	25.4	0.721	20.40	19.9	119.2	59.6	23.9	12.0
0.0015	38.1	1.082	30.60	29.8	178.8	89.3	35.7	18.0
0.0020	50.8	1.44	40.80	39.8	238.4	119	47.7	23.9

Source: G. DiBari (1993). Nickel Plating, Metal Finishing, Guidebook and Directory Issue, p. 229.

Solutions for Plating Baths

Types of Nickel Solutions - The most commonly used solutions are based on a mixture of nickel sulfate, nickel chloride and boric acid (Watts solution), and a sulfamate solution. The Watts solution is a simple and inexpensive plating bath that is easy to control and keep free from impurities. The sulfamate solutions, however, have certain advantages that make them extremely popular for electroforming. Nickel sulfamate solutions generate deposits that are low in stress, with high rates of deposition and high rates of thickness. All-chloride solutions are also used for a harder, stronger, and finer grain size of nickel deposits than is available from the Watts solutions. Solutions based on salts such as pyrophosphate and citrate have been used, but these solutions and the all-chloride solutions are of little industrial use.

The operating conditions and mechanical properties of deposits from several of the popular plating baths are noted in Table 2. Several other solutions exist that should be mentioned. The "Ni-Speed" process was developed by INCO to increase nickel deposition rates up to 1 mm per hour when current density is uniform. This allows operators to decrease production time – even on complex shapes, the deposition rate can be increased by two to three times over that of conventional processes. Other specialty baths include a barrel plating formulation, cold bath, hard nickel bath, and nickel phosphorus baths. (DiBari, 1993)

							Table 2	e 2										
	L	ypical	Compo	sitions, '	Operat of De	ting Cor posits fi	ndition: rom Se	perating Conditions and Approximat of Deposits from Several Electrolytes	oproxin ectrolyt	Typical Compositions, Operating Conditions and Approximate Mechanical Properties of Deposits from Several Electrolytes	ıanical	Propert	ies	:				
Constituents	Chic	All Chloride		Chloride Sulfate	A Fluot	All Fluoborate	A	All Sulfate	y Sulf	All Sulfamate	Chloride Sulfamate	ride mate	H	Hard Sulfamate	Wa	Watts	Hard Watts	d ts
					Typical	Electroly	te Compe	Typical Electrolyte Composition g / L (oz / gal)	/L (oz / 1	gal)								
Total Nickel	75	(01)	86.4	(11.5)	75	(10)	70	(9.3)	84	(11.2)	84	(11.2)	45	(9)	78	(10.4)	09	(8)
Nickel Chloride	300	(40)	158	(21)							22.5	(3)	7.5	Ξ	09	(8)	45	9)
Nickel Sulfate			188	(25)			330	(44)							300	(40)	292	(35)
Nickel Sulfamate									450	(09)	428	(57)	248	(33)				
Nickel Fluoborate					300	(40)												
Boric Acid	30	(4)	37.5	(5)	30	(4)	30	(4)	37.5	(5)	37.5	(5)	30	(4)	30	(4)	30	(4)
Anti Pitter	×		×		×				×		×		×				×	
Addition Agent													Q S S	Optional Stress Reducer			Optional Stress Reducer	onal ss cer
						o d	erating C	Operating Conditions										
Temperature °C (°F)	55	(130)	55	(130)	55	(130)	55	(130)	09	(140)	09	(140)	55	(130)	55	(130)	90	(122)
Hd	2.0		3.0		2.7		1.5		4.0		4.0		5.0		3.0		5.0	
Current Density, A/m³ (A/ft³)	540	(20)	240	(20)	320	(30)	400	(40)	540	(50)	540	(20)	009	(09)	540	(20)	540	(50)
						Me	chanical	Mechanical Properties				İ						
Tensile Strength, MPa (ksi)	069	(100)	517	(75)	400	(88)	480	(07)	413	(09)	758	(011)	968	(130)	413	(09)	1170	(170)
Hardness, DPN (100 g load)	240		230		150		170		061		300		470		150		350	
Elongation, % in 50.8 mm (2 inches)	14		20		30		28		30		5		9		28		2	
Internal Stress, MPa (ksi)	345	(50)	220	(32)	138	(20)	117	(17)	14	(2)	69	(10)	Va Acc to A	Variable According to Addition Agent	138	(20)	Variable According to Addition Agent	able ding Jition ent

Source: DiBari, G. (1993). Nickel Plating. Metals Finishing Guidebook and Directory Issue, p. 233.

The solutions for decorative nickel plating are distinct in that the baths also contain organic agents, such as benzene disulfonic acids, benzene trisulfonic acid, naphthalene trisulfonic acid, benzene sulfonamide, formaldehyde, coumarin, ethylene cyanohydrin, and butynediol. Generally, the temperature of nickel plating baths ranges from 45° to 65° Celsius (110° to 150° Fahrenheit). The current densities range from 270 to 1,075 A/m² (25 to 100 A/ft²). (USEPA, 1996)

2. Materials and Methods

A literature search and surveys were conducted to identify and collect all available nickel emissions testing reports or information for airborne nickel releases from nickel plating operations. A comprehensive literature search of several databases (listed in Appendix C) was conducted to identify and collect available emissions-related information for the nickel plating industry. Section 4 lists references for the documents cited, as well as other documents reviewed. The literature search was supplemented with survey calls to nickel plating associations, nickel plating operators, and regulatory agencies (see Appendices A and B). In addition, calls were made to approximately 50 nickel plating firms or service agencies and governmental agencies for the most current information (see Appendix D).

The literature was reviewed to collect information on the control devices and ventilation methods used in the nickel plating operations. None of the literature encountered had data on existing control equipment or required control equipment for nickel plating operations. Exhaustive calls were made to several associations in the industry as well as to USEPA and NIOSH. None of the conversations were fruitful other than to reiterate the earlier finding that no studies had been done that included control equipment for nickel plating and, according to EPA, there are no requirements for control equipment for nickel plating operations. As a result, the bulk of the information on control equipment that follows is gleaned from work (USEPA, 1993) on chromium emissions resulting from chrome electroplating and anodizing operations. This EPA report most closely resembled the information needed for this study.

To supplement the EPA data, calls were made to different firms in the industry as well as to industry research agencies. As much as possible, questions were asked to carefully define those chromium emission control devices and emission capture techniques that were applicable to the nickel plating operations.

Additional testing is recommended to better characterize emissions from nickel plating operations. The best documented emissions data available were provided by the MFASC and the SCAQMD, each of which conducted emissions source tests at a nickel plating facility in Santa Fe Springs, California during 1998. The source testing firm hired by MFASC, Pacific Environmental Services, Inc., (PES) prepared a detailed source testing protocol for this test (see Appendix E). Results from the MFASC test are included as Appendix F. The results of the SCAQMD test are included as Appendix H.

3. Results and Discussion

Control Technology

Sources of Information - The literature was reviewed to collect information on the control devices and ventilation methods used in the nickel plating operations. None of the literature encountered had data on existing control equipment or required control equipment for nickel plating operations. Exhaustive calls were made to several associations in the industry as well as to USEPA and NIOSH. None of the conversations were fruitful other than to reiterate the earlier finding that no studies had been done that included control equipment for nickel plating and, according to EPA, there are no requirements for control equipment for nickel plating operations. As a result, the bulk of the information that follows regarding electroplating emissions capture and control techniques is gleaned from work (USEPA, 1993) on chromium emissions resulting from chrome electroplating and anodizing operations. This EPA report most closely resembled the information needed for this study.

To supplement the EPA data, calls were made to different firms in the industry as well as to industry research agencies. As much as possible, questions were asked to carefully define those chromium emission control devices and emission capture techniques that were applicable to the nickel plating operations. As with any work, there were conflicts in information, even from the "experts," regarding which type of equipment was used in the nickel plating operations, types of control devices prevalently used, the need for control devices, and which equipment was most effective. The one fact that was agreed upon was that, most often, no control equipment was used in the nickel plating shops. If control equipment was in place, it was reported to be a lateral or push-pull exhaust system" or a mesh pad mist eliminator.

<u>Uncontrolled Emissions</u> - Mists are generated as a result of the plating process as hydrogen and oxygen gas evolve. The gas bubbles rise to the surface and may carry considerable liquid with them in the form of a fine mist. The release of gas is a function of the chemical or electrochemical activity in the tank. The rate of gassing depends on the activity in the tank (chemical/electrochemical increases with amount of work), the strength and temperature of the solution, and the current densities in the tank. The extent

^{*}Conversations with Ted Mooney, Dean High, Tom Miles, Dan Miles, Randy Solganik.

^{**}Conversation with Ted Mooney with Finishing Technology, December 1996.

^{****}Conversation with Dan Miles with Conserve Technology, January 1997.

of acid misting from the plating baths is dependent mainly on the efficiencies of the baths. Nickel plating baths have high cathode efficiencies so that the generation of mist is minimal. (USEPA, 1993) Only about 3% of the electrical current releases hydrogen at the cathode, and practically no oxygen is emitted at the anodes during the process.

According to a study by USEPA (1984), the emissions from plating shops occur during the handling of nickel salts used to prepare the solutions, the plating process, and the grinding, polishing, and cutting operations performed on the finished product and scrap metal. As mentioned above, hydrogen and oxygen gases are generated from the nickel salts and emitted as a mist during the plating process. However, EPA states that nickel emissions from misting are generally very low or nonexistent due to the low temperature and low current densities used in the nickel plating baths. Based on the high cathode efficiencies (95 to 98%) and baths operated at moderate temperatures and low to moderate current densities, nickel plating solutions containing sulfate and/or chloride exhibit low gassing. Thus, the need for local exhaust ventilation may be minimal due to these conditions. (USEPA, 1993, p. 3-15) In three studies cited by USEPA (1984, p. 98), the nickel air emissions were reported as negligible. Even those emissions that occurred during the grinding, polishing, and cutting were determined to be insignificant.

Further, a NIOSH study (1984) of five nickel electroplating baths at four facilities found very low concentrations of airborne nickel around unventilated nickel plating baths. Three of the tanks contained Watts nickel baths and two tanks contained nickel sulfamate. The tanks ranged in size from 370 to 1,680 gallons and none were covered, contained floating plastic balls, or were air agitated. Four of the tanks were mechanically agitated by other means. Area indoor air sample results for all five tanks showed extremely low nickel levels. The highest measurable nickel exposure was $6\mu g/m^3$ and the highest measurable tank-area concentration for nickel was $7\mu g/m^3$. Eight of 10 personal samples and 39 of 42 area samples were below the limit of detection. NIOSH concluded that the nickel exposure from unventilated nickel sulfate (Watts bath) and nickel sulfamate tanks is not a problem. Increased temperature (up to 160°) did not result in high nickel levels, confirming that plating baths tested did not need exhaust ventilation.

Source Test Method - ARB uses its Method 433 source test procedure to determine if nickel compounds are present in the exhaust from plating operations. In Method 433, particulate and gaseous phase nickel compounds are withdrawn isokinetically from the stack using a sample train and collected on a glass fiber filter, or in impingers that contain nitric acid. The typical detection limit for ARB Method 433 is 40 ug/L of solution analyzed. For the solution analyzed, the impinger catch, and the weak acid extract used for sample recovery of the sampling train, a typical listed working range for the method is between 300 ug/L and 5,000 ug/L. However, it should be noted that using Method 433 and the minimum detection limit of 40 ug/L, it would take 714 minutes, or 30 hours, to test for 7 ug/m³ of nickel compounds in the air above an unventilated nickel tank, such as the measurement made by NIOSH that is described in the previous paragraph. For the measurement of nickel present at lower concentrations or nickel that is present with compounds that interfere with the absorption of nickel, ARB approves equivalent procedures on a case-by-case basis. These include furnace atomic absorption spectrometry, argon plasma atomic emission spectrometry, neutron activation analysis, and x-ray fluorescence. Based on telephone calls to local air districts in California, ARB

Method 433 would be used to analyze nickel plating emissions in each individual district, unless the facility proposed a source test method that was equivalent and would meet ARB's approval. Most of the California districts are not equipped to perform Method 433 and would require the facility to perform any required testing using an approved source test contractor. Doug McClure of the Bay Area Air Quality Management District (BAAQMD) Technical Division indicated that the BAAQMD would either perform the source test, or require the facility to use an approved source test contractor.

For nickel emissions from plating operations, the available EPA test methods are a modified Method 5, "Determination of Particulate Emissions from Stationary Sources," combined with a modified Method 12, "Determination of Inorganic Lead Emissions from Stationary Sources," (40 CFR 60, App. A). Similar to ARB Method 433, these EPA methods collect the samples with a Method 5 train that includes a weak acid in the impingers, and extract the samples with a weak acid followed by analysis by atomic absorption spectrometry.

The literature review revealed a scarcity of source test data for nickel plating operations. Table 3 summarizes eight documents located by the literature review. Of the eight documents listed in Table 3, only seven include source test reports, and only three (the 1998 Foss Plating test by PES and the two SCAQMD tests) provide sufficient process data necessary to develop meaningful emission factors.

Table 3 Sources of Nickel Plating Test Data				
Description	Reference	Report		
Air Toxics Technical Assistance for the State of Alaska	EPA Region X	no (Dickson et al, 1987)		
Deutsch Engineered Connecting Devices	USEPA, RTP	yes (Kleinfelder, 1991)		
California Fine Wire (results not tied to nickel process rate data)	San Luis Obispo County APCD	yes (Air _x Testing, 1995)		
Deutsch Engineered Connecting Devices (results not tied to nickel process rate data)	Pacific Env. Services	yes (Air _x Testing, 1996)		
Kaynar Technologies	Pacific Env. Services	yes (PES, 1998)		
California Technical Plating Company	South Coast AQMD	yes (SCAQMD, 1998)		
Foss Plating Company	Pacific Env. Services	yes (PES, 1998)		
Foss Plating Company	South Coast AQMD	yes (SCAQMD, 1998)		

Due to the lack of nickel source test data, and as part of its industry effort to work with ARB, MFASC conducted an emissions source test at the Foss Plating facility in Santa Fe Springs, California during the second quarter of 1998. MFASC hired PES to perform the

source test. PES prepared a source test protocol that was reviewed and approved by ARB (see Appendix E for protocol and response to comments). Test results are summarized later in this section (see Table 6), and the source test report prepared by PES is included as Appendix F to this report.

The SCAQMD conducted a source test at the same Foss Plating facility in October 1998. This test was designed to address issues raised by the SCAQMD regarding high levels of background nickel and potential fugitive losses during the MFASC testing. The source test report prepared by the SCAQMD is included as Appendix H to this report.

The SCAQMD also conducted a source test at California Technical Plating in September 1998. MFASC expressed concerns that the plating tank used during this test was not representative of typical nickel plating operations. The SCAQMD's October test at Foss Plating was also meant to address validity concerns raised as a result of these September tests at California Technical Plating. A table summarizing the results of testing at California Technical Plating is included as Appendix I to this report.

Emission Capture Techniques - Based on the literature, several methods are available for the capture and control of nickel emissions during plating operations. As with most electroplating processes, local exhaust ventilation is the most common method used to capture the mist from nickel plating baths. Access to the plating tanks requires the use of equipment that does not restrict the plating activity. As such, canopy hoods and enclosures are generally not used. More common is the capture of nickel emissions using lateral (slot) and push-pull exhaust hoods. Where no drafts exist, the recommended capture air velocity across the liquid surface of the tank is 46 m/min (150 ft/min) for contaminants with high hazard potential and a high rate of mist evolution, such as chromic acid. (USEPA, 1993) The design ventilation rate depends on the hood type, the control velocity selected, and the width-to-length ratio of the tank. Table 4 lists the recommended ventilation rates for tanks with aspect ratios (width-to-length) less than 2.0 (USEPA, 1993, p. 4-3) If the aspect ratio exceeds 2.0, the option to ventilate parallel to the long dimension of the tank is not practicable. (USEPA, 1993, p. 4-2) Although the ventilation rates in Table 4 are the parameters for capturing chromic acid mist, calls made to the American Industrial Hygiene Association verified that "all other things being equal, the parameters should be about the same for ventilating nickel mist."

Correspondence with Heather D. Borman, Industrial Hygienist, State Compensation Insurance Fund, dated January 1, 1997.

Table 4 Minimum Ventilation Rates for Ventilation Hoods Used to Capture Emissions of Chromic Acid Mist from Chromium Plating and Chromic Acid Anodizing Tanks ²								
Hood along one side or two parallel sides of tank when tank is against wall or baffled Hood along one side or two parallel sides free-standing tank not against wall or baff								
Tank Width-to- Length Ratio	m³/n	l Hoods nin/m² in/ft²) ^{bc}	m³/m	ıll Hoods nin/m² nin/ft²)	m^3/m	Hoods in/m² n/ft²) ^{bc}	m³/r	ull Hoods nin/m² nin/ft²)
0.0 - 0.09	46	(150)	23	(75)	69	(225)	35	(115)
0.1 - 0.24	58	(190)	26	(95)	76	(250)	38	(125)
0.25 - 0.49	69	(225)	35	(115)	76	(250)	38	(125)
0.5 - 0.99	76	(250)	38	(125)	76	(250)	38	(125)
1.0 - 2.0	76	(250)	38	(125)	76	(250)	38	(125)

- Ventilation rates are based on the minimum control velocity of 46 m/min (150 ft/min) recommended for chromic acid mist.
- For lateral hoods along centerline or two parallel sides of tank, tank width-to-length ratio equals tank width +2.
- Although a ventilation rate of 76 m³/min/m² (250 ft³/min/ft²) may not produce a control velocity of 45 m/min (150 ft/min) at all aspect ratios, the ventilation rate is considered adequate for control. Source: U.S. Environmental Protection Agency (1993), p. 4-3.

Lateral Exhaust Systems - For all solution tanks where the air movement is horizontal into a hood that does not project over the entire tank, the ventilation is said to be laterally exhausted. The control of the mist off the open-surface solution tanks is accomplished using both single-sided and double-sided slot hoods. The airflow distribution is dependent on the slot velocity; the recommended slot velocity is 610 m/min unless takeoffs (openings where emissions are exhausted to the duct) are provided. The required slot velocity may be lower depending on the design of the takeoff. For tanks at least 1.8 m (6.0 ft) in length, multiple takeoffs are recommended; for tanks at least 3.0 m (10 ft), multiple takeoffs are required to maintain good capture efficiency (USEPA, 1993, p. 4-2). The lateral slot hood is advantageous when the air distribution is over a large surface but minimal space is occupied by the hood. The disadvantage is the relatively high static pressure loss at the hood entry when the slot velocity is high.

For tanks with 107 cm (42 in.) width or greater, the push-pull ventilation is recommended. An exhaust hood located at one side of the tank is the receptacle for air that is pushed across the width from the opposite side via slots, orifices, or nozzles. The ventilation efficiency of the push-pull system is the same as the lateral exhaust system while only about one-half the volume of air is used. As a result, the operations use smaller air handling equipment and have lower utility and makeup air requirements. The limits of the push-pull system are seen where plating racks, anode bars, or other obstructions interfere with the flow of the push air across the tank. With any obstructions, the push-pull system cannot be used.

Several factors affect the performance of local exhaust ventilation. A major factor is the maintenance of an adequate ventilation rate at a level sufficient to capture and convey the

contaminated air to the exhaust hood. The air movement must occur in a uniform, horizontal movement across the tank at a rate sufficiently high to compensate for any air disturbances across the tank due to cross drafts. The makeup air supply is another factor affecting the ventilation. Replacing or offsetting the air exhausted from the building allows the exhaust systems to work without having an increase in static pressure due to the negative pressure or suction in the building. The volumetric flow of the makeup air is dependent on the layout and siting of heat sources and the physical layout of the building relative to the tank location. For the push-pull system, additional factors apply. The amount of push air supplied, the size of the exhaust hood installed, and the extent to which obstructions are present in the air stream path are all factors that affect the performance of the system.

Emission Control Techniques - Based on a review of the literature, controlling emissions from chromic acid mist resulting from the electroplating and anodizing operations can be accomplished using several proven control devices. Most frequently the mist is controlled using mist eliminators and wet scrubbers. The following discussion of control techniques of emission controls is based on USEPA (1993), except where noted otherwise.

Mist Eliminators - The mist eliminators collect the mist from the gas stream by using inertial impaction and direct interception. Inertial impaction collects the droplets as large particles that collide with a stationary surface. Direct interception utilizes a fluid layer on the collection surface that intercepts the flow of the mist particles. For both inertial impaction and direct interception, the collected droplets drain to the bottom of the collection device. Although operated as dry units, the devices are periodically flushed with water to keep the collection surfaces clean.

Chevron-blade mist eliminators work with a horizontal flow configuration of one or more sets of parallel, chevron-shaped blades. The control of the mist occurs by changing the direction of the flow of the gas four times for each blade. The droplets adhere to the surface of the blades due to the inertial force. Washing the blades periodically releases the built-up particles. To prevent the water droplets from being drawn through the stack, the fan must be turned off during the washing. As the blades are washed, the wash water is then drained to the plating tank or to a wastewater treatment system. The most common blade designs are overlapping and sinusoidal wave. The overlapping edges of the overlapping design and the catchments of the sinusoidal design serve as collection troughs for droplets and promote drainage of the droplets in the collection sump. The performance of the chevron-blade mist eliminators depends on the face velocity of the gas stream across the blades, the spacing between blades, the tightness of seals between the blades and the walls of the unit, and the frequency of washing the blades. Control device vendors estimate that removal efficiencies range from 80 to 90 percent. (USEPA, 1993, p. 4-12)

Mesh-pad mist eliminators consist of layers of interlocked filaments densely packed between two supporting grids. The multiple layers are compacted and connected by thin filaments. The mesh pads are designed with three layer patterns: (1) layers with a crimp in the same direction, (2) layers with a crimp in alternate directions, and (3) spiral-wound layers. For particles larger than 3 um (0.12 mil) moving with sufficient velocity, inertial

impaction occurs as the particles strike the filaments and adhere to their surface. The smaller particles collide with the filaments as a result of the surface fluid layer. Droplets are formed and drain to the bottom of the mist eliminator due to gravity. The control device efficiency of the mesh-pad mist eliminator is estimated at 96 to 99%. (USEPA, 1993, p. 4-15) The disadvantage of this type of mist eliminator is the tendency of the pad to plug. The performance of the pad is also affected by the velocity of the gas stream and the particle size.

Scrubbers - Scrubbers are control devices used in the control of emissions from chromic acid mist from chromium plating and chromic acid anodizing operations. Several types of scrubbers exist: single and double packed-bed, fan-separator packed-bed, and centrifugal-flow. The single and double packed-bed scrubbers are utilized most often in the plating operations of chrome. The removal efficiencies range from 95 to 99% for the different types of packed-bed scrubbers. The removal of the chromic acid mist occurs by reducing the velocity of the gas stream at the scrubber inlet to increase the efficiency of the particle impingement. The mist droplets are enlarged by water sprayed perpendicular to the gas stream, causing the droplets to settle to the bottom of the scrubber due to gravity. The flow of the gas stream continues through the packed bed. The droplets impinge on the packing material that is continuously washed with water from spray nozzles. With the constant spray of water, the droplets are washed to the bottom of the scrubber. For the single and double packed-bed scrubber systems, the scrubber is followed by a mist elimination section downstream from the packed-bed to collect any water carryover. Most often, the chevron-blade mist eliminator is used.

Several factors affect the performance of the packed-bed scrubber. The major factors are the liquid-to-gas (L/G) ratio and the superficial gas velocity entering the packed bed. If the L/G ratio is too high, the gas flow is restricted when the packed bed becomes flooded. If the ratio is too low, the bed is not sufficiently wet and the interception of the particles by the fluid surface is inhibited. The lower collection efficiencies of a low L/G ratio also result from the particles not being wetted enough to enlarge and to adhere to the surface. The gas stream velocity must be sufficiently high to cause the enlarged droplets to collide with the packed bed. A velocity too high will cause the re-entrainment of the droplets and result in a decrease in the collection efficiency. The distribution of the packing media and the surface contact area of the packing media also affect the performance of the scrubber. Plugged spray nozzles and excessive buildup of chromic acid on the packing material can reduce the efficiency of the packed-bed scrubber.

Wetting Agents - Wetting agents are used primarily to reduce the surface tension of the plating baths. For chrome plating operations, there is a reduction in chromic acid emissions with the addition of a wetting agent. For surface tensions below 30 to 40 dynes/cm, the emissions are significantly lower than for surface tensions above this level. In addition, wetting solutions are utilized to control the formation and collapse of the hydrogen bubbles in order to get a smooth finish. (Warner, 1990) No control efficiency data were available for the use of wetting solutions alone; however, control efficiencies exceeding 99% are reported for wetting agents used in conjunction with foaming agents. (USEPA, 1993, p. 4-33) Foaming agents cause a foam layer to form over the plating bath, and this foam layer entraps any mist generated by the plating operation.

<u>Polypropylene Balls</u> - Polypropylene balls are used in the plating baths, floating on the surface to reduce heat loss, evaporation, and misting. Their use is limited due to certain factors. For automatic operations, the effectiveness of the balls is reduced as the balls are sometimes dragged out by the plating racks. Their usefulness in reducing misting is also inhibited by the fact that the balls tend to be pushed away from the anodes and cathodes where the surface of the bath is agitated by gassing. Polypropylene balls are estimated to control plating emissions by 68 to 82%. (USEPA, 1993, p. 4-33)

Cost Analysis

EPA Data - The cost analysis reviewed for this study (USEPA, 1993) included cost information based on several model plants with hard and decorative chromium electroplating and chromic anodizing operations. The cost estimates were presented for each of the control options and capital and annualized costs were estimated. The cost information for new operations was obtained from several vendors, with each vendor quoting a cost estimate based on the parameters of each model plant. Capital costs for ventilation systems, including exhaust hoods and ductwork, were reported separately from the control device estimates. The installation of the ventilation systems was based on OSHA requirements for chromium emissions in the workplace.

For each piece of equipment for a new operation, a complete analysis was conducted. The capital costs included the purchase cost of the control device and auxiliaries, direct installations costs, indirect costs and startup costs. The annualized cost involved direct operating costs such as utilities, labor and materials, indirect operating costs, and capital recovery costs.

A cost analysis of retrofitting existing operations was also estimated for each piece of control equipment. Data from the vendors included retrofit costs such as the modification of equipment as well as the removal and disposal of any existing control device. The actual cost of retrofitting varied depending on the specific facility, the layout and the existing control equipment. A scaling factor of 20% of the installed capital costs of control for new facilities was used to estimate the retrofit capital costs for existing facilities. To cover the cost of disposal and transportation, 5% of the vendor estimate was included. The annualized retrofitting costs for some of the control equipment were higher than costs for new facilities due to the higher capital recovery costs and higher indirect costs. Table 5 summarizes the 1993 USEPA cost data.

Table 5 Summary of 1993 USEPA Emission Control Cost Data for Hard Chromium Plating Model Plants ⁽¹⁾				
Control Option Small Plant ⁽²⁾ Medium Plant ⁽²⁾ Large Plant ⁽²⁾				
Chevron Blade	Capital Cost =	\$22,500	\$45,400	\$91,000
Mist Eliminator (single blade set)	Annualized cost =	\$4,800	\$8,500	\$15,100
Chevron Blade	Capital Cost =	\$23,800	\$49,800	\$99,700
Mist Eliminator (double blade set)	Annualized cost =	\$5,500	\$10,200	\$20,100
Single Packed-Bed	Capital Cost =	\$36,700	\$74,200	\$148,400
Scrubber	Annualized cost =	\$9,800	\$18,700	\$39,000
Mesh-Pad	Capital Cost =	\$23,000	\$66,000	\$124,900
Mist Eliminator	Annualized cost =	\$8,000	\$24,100	\$52,600
Fume Suppressants	Capital Cost =	\$0	\$0	\$0
(wetting agents and foam blankets)	Annualized cost =	\$1,000	\$3,300	\$17,200
Ventilation Hoods,	Capital Cost =	\$9,490	\$32,360	\$64,710
Takeoffs, and Ductwork	Annualized cost =	Not Listed	Not Listed	Not Listed

Note: 1) Data from USEPA, 1993, Tables 7-5 through 7-9, 7-15, and 7-40.

<u>Industry Information</u> - As shown previously in Table 2, the nickel plating industry uses a variety of chemistries to apply surface finishes to substrates; in addition, the process and equipment configurations vary from one facility to another. The required plated surface characteristics, the size of the plated part, and the available facility space contribute to the variations in the plating equipment between facilities. These variations and the emission standard to be achieved result in the fabrication of custom systems, and therefore result in site-specific control costs.* Several vendors were contacted and provided the same response. For general purposes, the following base cost data were obtained for one prefabricated packed-bed scrubber and one booster fan (Air Chem Systems, Inc., 1997).

Flowrate	Cost
2,000 cfm	\$24,300
5,000 cfm	\$27,100
10,000 cfm	\$36,000
20,000 cfm	\$54,600

Not included in the above cost data are capture equipment (e.g., plenum, ducts), engineering design, construction, or chemicals.

²⁾ Per USEPA, a "small plant" includes one plating tank and a 12,000 cfm blower. A "medium plant" includes four plating tanks and a 35,000 cfm blower. A "large plant" includes eight plating tanks and two 35,000 cfm blowers.

^{*} Conversation with Frank Hoffman with Calfran International, March 1997.

Developing Emissions Factors

In conversations with industry representatives,* suggestions were made as to the development of appropriate emissions factors based on the activity in the plating bath. Several factors were suggested: one emission factor that accounts for air agitation of the plating bath, which occurs at intervals during the nickel plating process; two emission factors for the plating process of electrolytic nickel plating depending on the type of plating solution; and a separate factor for electroless nickel processes.

<u>Factors Affecting Emissions</u> - Several factors are discussed in the literature as affecting emissions in nickel plating operations: the current density applied, the surface area of the part plated, the plate thickness, and plating time. Other factors are the type of part to be plated, the orientation of the part in the tank, the surface tension of the plating bath and the plating bath solution itself. In addition, for nickel plating tanks where agitation occurs, the agitation, whether mechanical or air, affects the emissions.

Plating Emissions Factors - A review of the available source test results and literature resulted in eight documents reporting nickel emission factors (see Table 3). However, only six of these reported emission factors are tied to nickel process rates. [Note: all units shown are as published, and for comparison purposes are converted to mg/A-hr.] The first emission factor was compiled from a 1987 report to USEPA. (Dickson et al, 1987) The emission factor was reported for nickel "strike" but is noted as being viable for nickel plating, where the source is the entire process of nickel electro-deposition. The 1987 report defines nickel "strike" as "an electrodeposition operation in which a very thin film of metal is plated into a base material to facilitate further plating with another metal or with the same metal." The emission factor value is reported as 2.25 x 10E-4 g/A-hr (0.225 mg/A-hr). USEPA converts this factor to units of lb/A-hr and reports it as 4.95 x 10E-7 lb/A-hr. (USEPA, 1990, p. 228)

The second emission factor was collected from a 1991 air toxics sampling report at Deutsch Engineered Connecting Devices. (Kleinfelder, 1991) The emission factor reported by EPA for this test is 0.63 grains/A-hr for uncontrolled nickel emissions. (USEPA, 1996, p. 12.20-17) This converts to 40.8 mg/A-hr.** However, the 1991 Deutsch test actually included six sample runs (two separate tests) measuring nickel emissions upstream of a packed bed scrubber, and six sample runs (two separate tests) measuring nickel emissions downstream of a wet scrubber. The nickel emission factor reported by Kleinfelder for the Deutsch source test was 26.4 mg/A-hr for controlled nickel emissions.

A third nickel emission factor was identified from an April 1998 source test performed by PES at Kaynar Technologies in Fullerton, California. This test reported nickel emission factors of 0.652 mg/A-hr for uncontrolled nickel plating, and 0.116 mg/A-hr for controlled nickel emissions from a horizontal packed bed scrubber.

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^{*} Conversations with Randy Solganik, Dean High and Tom Miles.

^{**} The equation used to generate equivalent units in milligrams/A-hr is (0.63 grains/A-hr x 64.8 mg/grain).

The fourth set of nickel emission factors identified is from an emissions test conducted by MFASC at Foss Plating in Santa Fe Springs, California during April and May 1998. This test reported nickel emission factors of 0.0496 mg/A-hr for nickel plating with air agitation, and 0.0239 mg/A-hr for nickel plating without air agitation (see Appendix F). These factors are well documented and the test report provides all necessary supporting data. However, significant background concentrations of nickel were measured at the Foss Plating facility, and this background nickel may have confounded the emissions test results. Also, the SCAQMD raised concerns regarding potential fugitive losses during the test, and the ARB raised concerns regarding chromium interference affecting the MFASC test results. (The laboratory that performed the nickel analyses for the MFASC test concluded that chromium concentrations were well below levels that would cause interference with the nickel test results; see Appendix F, page 21). Data from the Foss Plating test report are summarized in Table 6.

Table 6 Summary of Source Test Results Foss Plating Company				
With Air Agitation Without Air Agitation Background				
Sample Volume (DSCM)	2.146	2.119	2.222	
Sample Volume (DSCF)	75.797	74.825	78.458	
Nickel Sample Collected (ug)	43.7	23.3	10.7	
Stack Flow (DSCFM)	5,972	5,657	6,025	
Process Rate (A-hr/hr)	4,230	4,485	0	
Nickel Concentration (mg/DSCM)	0.0203	0.0111	0.0049	
Nickel Emission Rate (mg/hr)	207.2	106.4	49.8	
Nickel Emission Factor (mg/A-hr)	0.0496	0.0239	N/A	

The SCAQMD conducted its own test at the Foss Plating facility in October 1998 in an effort to address issues raised during the MFASC test. The SCAQMD test resulted in an emission factor of 0.214 mg/A-hr for nickel plating with air agitation, and 0.369 for nickel plating without air agitation (see Appendix H). The SCAQMD tests were conducted with a cover over the plating tank to prevent background contributions, and plated parts were not removed from the tanks during the test to simulate drag-out effects. Also, only one test run was completed with air agitation during nickel plating, and the runs without air agitation utilized unusually low nickel solution concentrations, causing increased bubbling and increased nickel emissions. The SCAQMD results for nickel plating with air agitation were about four times higher than the MFASC results, and the SCAQMD factors without air agitation were about 15 times higher than the MFASC results.

The SCAQMD also conducted a source test in September 1998 at a nickel plating operation at California Technical Plating Company. These tests resulted in a nickel emission factor of 0.251 mg/A-hr for nickel plating with air agitation, and 0.090 for nickel plating without air agitation (see Appendix I). The tests were conducted on a fully enclosed 3 ft. by 5 ft. nickel plating tank, which is smaller than typical nickel plating tanks. Concerns were raised by MFASC regarding the representativeness of this plating operation; however, subsequent testing by the SCAQMD at Foss Plating resulted in a similar nickel emission factor for plating operations with air agitation.

Finally, the SCAQMD has reported an emission factor for elemental nickel emissions from bright and semi-bright nickel plating of 7.20 x 10⁻⁸ lb/A-hr. (SCAQMD, 1996) Converting this value to milligrams/A-hr results in an emission factor of 0.0327 mg/A-hr. This SCAQMD factor is not based on test data, but rather is based on a CARB chrome plating emission factor (5.2 mg/A-hr) adjusted to account for differences in nickel plating tank solution concentrations and cathode efficiencies.

Two other source tests identified previously in Table 3 (California Fine Wire in 1995 and the 1996 Deutsch test) did not include process rate data and simply reported nickel emissions in units of pounds per hour. Therefore, these data are not useful for developing nickel emission factors. Table 7 compares the results of the referenced source tests and SCAQMD emission factors.

Table 7 Comparison of Reported Nickel Emission Factors			
Emission Factor Source	Emission Factor (mg/A-hr)		
Deutsch 1991 Uncontrolled (1996 EPA AP-42)	40.8		
Deutsch 1991 Controlled (1991 Kleinfelder Report)	26.4		
Kaynar 1998 Uncontrolled (1998 PES Report)	0.652		
SCAQMD 1998 Foss Plating without Air Agitation	0.369		
SCAQMD 1998 Cal Technical Plating w/Air Agitation	0.251		
Dickson, et al, 1987, for Nickel "Strike"	0.225		
SCAQMD 1998 Foss Plating with Air Agitation	0.214		
Kaynar 1998 Controlled (1998 PES Report)	0.116		
SCAQMD 1998 Cal Technical Plating w/o Air Agitation	0.090		
Foss Plating 1998 with Air Agitation (1998 PES Report)	0.0496		
SCAQMD Calculation based on Chrome Plating	0.0327		
Foss Plating 1998 w/o Air Agitation (1998 PES Report)	0.0239		

As indicated in Table 7, there is a wide variation between the listed nickel emission factors. However, only the MFASC and SCAQMD Foss Plating test results can be accurately verified based on data presented in the source test reports. The Deutsch and Kaynar reports do not provide adequate process data to confirm the process rates used, and the Deutsch report does not provide lab results of captured nickel quantities which can be correlated to the nickel emission factors presented in the report. No data was available to support the Dickson emission factor, and the SCAQMD calculated factor is not based on source test data. Furthermore, the Deutsch test results used by EPA in developing its AP-42 emission factor for nickel plating (40.8 mg/A-hr) are higher than EPA's AP-42 factor for hard chromium electroplating (7.78 mg/A-hr). This is inconsistent with expected results because nickel plating has a much higher cathode efficiency than chromium electroplating, resulting in much lower hydrogen gas formation at the nickel plating cathode and subsequently less misting at the tank surface. This surface misting is a significant factor affecting electroplating emission rates. (USEPA, 1993)

The MFASC and SCAQMD Foss Plating test reports, and the SCAQMD California Technical Plating test report, all presented sufficient data to verify the reported nickel emission factors. However, it is recommended that additional source test data be collected to better reconcile the differences between the two Foss Plating results, and between the Foss Plating and California Technical Plating results. Any additional source tests should accurately track process data during the source test periods, should isolate the nickel plating tanks to minimize the background nickel contribution to the nickel plating emission factor, and should provide all lab analyses of nickel emissions captured during the test run. A model source test protocol for conducting additional emissions testing has been provided as Appendix G. This model protocol is based on the MFASC Foss Plating test protocol prepared by PES. PES estimates that a typical three-run nickel source test costs approximately \$5,000, not including any costs for vapor collection sheeting and ducting, or forced draft ventilation systems. A typical test may require one to two weeks for set up, one day to sample, two weeks for lab analyses, and two weeks for final report preparation.

Exposure Measurement and Data

No information for nickel concentrations from plating operations at a facility property was located during the literature review. While 42 nickel plating facilities underwent an AB2588 review, the use of these data does not ensure the emissions from nickel plating operations have been adequately assessed. Therefore, unless the nickel plating exposure rates estimated for the AB2588 program were based on a nickel plating source test that included plant process data, these AB2588 exposure data are not shown in this section of the literature review.

EPA's Industrial Source Complex (ISC3) and SCREEN3 Models are available to perform an ambient exposure assessment for emissions of nickel from nickel plating operations at the property line.

Workplace exposure data were located. According to a study by Crawford (1996a), nickel exposures in the workplace are unknown due to a lack of resources to measure exposure. However, notes Crawford, data from various nickel plating operations are detailed in a health guide published jointly by the Nickel Producers Environmental Research Association (NiPERA) and the Nickel Development Institute (NiDI) (1994). The available data from several nickel plating operations indicate that, while some parts of the nickel plating operations exceed regulations, exposures generally are lower and in compliance with regulations overall. (Crawford, 1996a, p. 66)

Exposure Limits - The permissible exposure limits are different, though similar, from one country to the next. For the United States, the limits set by OSHA are 1 mg/m³ for nickel metal and insoluble nickel compounds and 0.1 mg/m³ for soluble compounds. However, the 0.1 mg/m³ value was rescinded because it had been improperly established. As a result, the only permissible exposure limit for nickel and any of its compounds, except for nickel carbonyl, is 1 mg/m³. (Crawford, 1996a)

The American Conference of Governmental Industrial Hygienists (ACGIH) has put nickel soluble compounds on the "Notice of Intended Changes List for 1996." The intended change was to lower the Threshold Limit Values (TLVs) for nickel and all its compounds to 0.05 mg/m³. The TLV has been opposed by the NiDI and the NiPERA. A revision of the intended change has been proposed: 0.5 mg/m³ for nickel metal, 0.1 mg/m³ for insoluble nickel compounds, and 0.05 mg/m³ for soluble nickel compounds. (The intended TLV of 0.05 mg/m³ for the soluble nickel compounds is the same TLV for hexavalent chromium set in 1994.) The ACGIH has listed nickel oxides, subsulfides, and nickel carbonyl as confirmed human carcinogens. It is likely that the ACGIH will propose that nickel and all its compounds be classified as confirmed human carcinogens. (Crawford, 1996a) Both NiPERA and NiDI dispute the inclusion of the other nickel substances based on current evidence.

Nickel as an Alternative

The toxic effects of chromium coatings have caused a search for an alternative metal coating. A patented nickel-tungsten-silicon (Ni-W-SiC) composite electroplating process is being considered as an alternative to replace functional (hard) chromium coatings. Although the Ni-W-SiC process has several benefits, the primary concern is that, as a substitute, the nickel-tungsten process contains ingredients that have similar health and environmental concerns as chromium. The allergenic character and carcinogeneity of specific nickel compounds is noted in several studies. (Crawford, 1996a; Simon, 1994; Darby, et. al., 1978) In addition, the increased efficiency of the plating solution of the Ni-W-SiC process with regard to plating speed must be balanced with the fact that the solution produces a wastewater that requires treatment and that the solutions are subject to biological decomposition (USEPA, 1994). In fact, the real and alleged effects of nickel on the environment and human health have caused some surface finishers to search for alternatives to nickel plating (Simon, 1994).

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